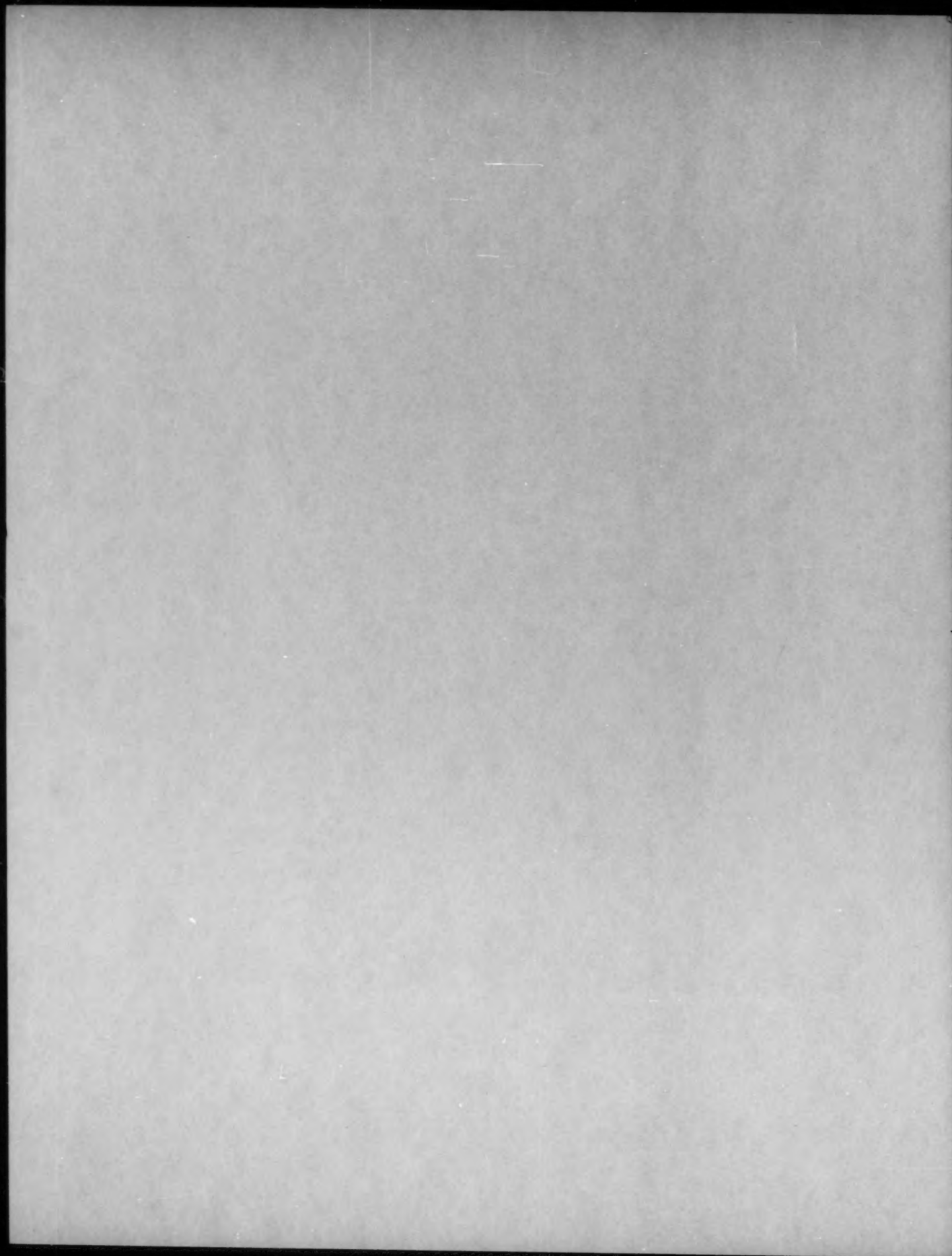


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SCIENCE USSR**

Vol. 2 No. 2 1953



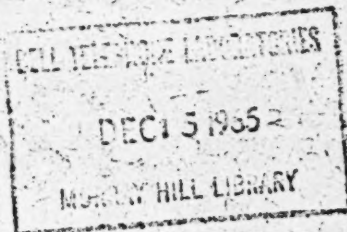
BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
DIVISION OF CHEMICAL SCIENCES

1953

Number 2

March-April

IN ENGLISH TRANSLATION



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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
DIVISION OF CHEMICAL SCIENCES

1953, No. 2

March - April

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IN ENGLISH TRANSLATION

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GEOMETRIC ISOMERISM AND PROPERTIES OF COMPLEX COMPOUNDS

L. I. Chernyshev

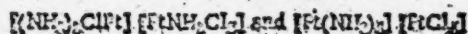
From the point of view of a chemist investigating complex compounds and therefore accustomed to working with the concept of the central atom, the difference in properties between ordinary structural isomers follows quite naturally from general chemical ideas concerning the undoubted and necessary dependence of the properties of a substance on its structure. If we take any example of isomerism, say butane-isobutane, then actually, no carbon atom can be found in one isomer that has an inner sphere identical in composition with the inner sphere of a carbon atom of the other.

Let us examine, as an example, the second carbon atom in the butane molecule $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$ and compare the composition of its inner sphere with that of the inner sphere of the second carbon atom in the isobutane molecule



It will be seen that in butane the inner sphere is composed of methyl, methylene, and two hydrogen atoms, whereas in isobutane there are three methyls and a hydrogen. Hence, in this case it is quite immaterial what we take as our basis in explaining the difference in the chemical reactions of the isomers: the central atom concept, or the concept of the differentiation of the molecules, each considered as a whole. A distinction in chemical properties is obtained, independently of the way in which we regard the structure of the molecules. Thus, the difference in the chemical behavior of the two isomers is not at all surprising, but appears, on the contrary, to be less than would be expected, for in the whole butane molecule it is impossible to find a carbon atom having an inner sphere of identical composition with that of any of the carbon atoms of the isobutane molecule. This equivalence between the approach from the point of view of the composition of the inner sphere of a central atom and the usual method of organic chemists—the determination of the degree of chain-branching and of the distribution of bonds—is altogether to be expected, for the theory of the structure of complex compounds is in essence a development of the same Eilertsen theory of structure. However, with the assumption that the differing behavior of isomers depends only on the composition of the inner sphere, the possibility of explaining this difference in behavior on the basis of the mutual effects of atoms composing the molecule moves into the background, for it may be found that this difference in the composition of the inner sphere is quite sufficient to explain the differing behavior of isomers.

If we take an analogous example from complex compounds, then it is quite obvious that the following isomers



will differ greatly in their chemical behavior, quite independently of the presence or absence of any mutual effects between atoms entering into the inner sphere of the complex. Sufficient cause for their differing behavior is to be found in the fact that the first salt dissociates into singly charged ions, whereas the second gives two doubly charged ions—a difference that is of the same order as that between two carbon compounds containing a double and single bond respectively. On the other hand, the difference in properties may nevertheless depend, in the isomers that we have examined, on the differing spatial arrangement of atoms in the molecule, which in the organic isomers leads to a different degree of chain-branching, and in the complex compounds to a differing spatial arrangement of bonds with the central platinum atom.

To define the extent to which the difference in properties in these isomers is to be attributed to differences in build-up and the extent to which it is to be attributed to differences in spatial arrangement is at present quite impossible, and the only approach to this problem is a study of the difference in properties of geometric isomers. In this particular case of isomerism the whole of the difference in properties must arise from purely spatial causes. However, for many properties this difference is not very great, which, at a first glance, suggests comparison with optically active enantiomorphs, which differ from one another only in the sign of rotation. The cause of the absence of a distinction in properties between stereoisomers is clear: no work is expended in the process of converting one stereoisomer into the other, and the energies of the stereoisomers are therefore identical.

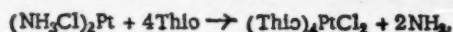
It has been found that the difference in energy between the geometrically isomeric diammines of bivalent platinum—the simplest example of geometric isomerism and the one that was first discovered—is about 3 kcal per mole (V. A. Palkin's determinations). This energy may be regarded as the heat of conversion of one isomer into the other, and the sign of the heat of conversion is in accord with the requirements of electrostatics: 3 kcal is evolved in the conversion of the cis-diammine into the trans-diammine.



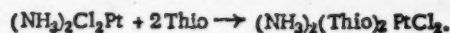
As will be seen from the diagram, this change is accompanied by a separation of the negative charges from one another, which naturally leads to evolution of heat. The thermal curves of the cis and trans isomers give further confirmation of the greater thermal stability of the trans isomer: its decomposition begins 50° higher than that of the cis isomer. In the case of cobalt compounds the isomers are appreciably different in color; the platinum isomers do not differ so much: the trans compound is generally somewhat lighter in color. The ultraviolet absorption spectra of solutions show a difference marked not so much by a change in character as by a regular displacement of the absorption curves (A. V. Babaeva).

There is an appreciable difference in the dipole moments which is always in accord with the accepted structure, the cis isomers having higher dipole moments than trans isomers. There is a difference, not very great, also in dielectric constant. The difference in refractive index is again not very great, but it may be used for determining the configuration. The crystal structure, as determined by the aid of X-rays, while confirming the different disposition of inner-sphere substituents in geometric isomers, does not reveal any particular difference in their distances from the central atom. The melting points are different, but the differences are not very great—not hundreds of degrees, but ten or so at the most. There are appreciable differences in solubility (the trans compound is generally not as soluble as the cis), for in the process of dissolving a chemical reaction occurs and the differences between geometric isomers become quite notable in chemical reactions. Geometric isomers of platinum possess, in fact, a property that permits them to be readily distinguished from one another: the differing speeds of the chemical reaction of displacement in the inner sphere and the resulting difference in type of chemical reaction.

We will cite some examples. As Kurnakov showed, sixty years ago, thiourea reacts with cis-dichlorodiammines, giving tetrathiourea derivatives according to the equation:



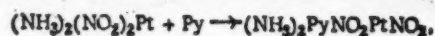
and with trans-dichlorodiammines, giving mixed trans derivatives according to the equation:



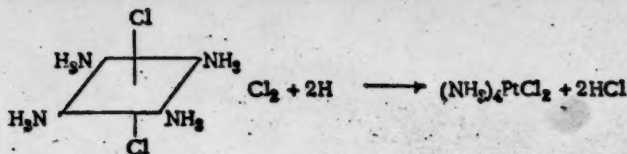
In the first case ammonia is displaced by the urea, and in the second case this does not occur (thiosulfates and sulfites react with diammines in a similar way). Nitrodiammines show the same difference when reacting with amines. Thus, when the cis-dinitrodiammine reacts with pyridine, ammonia is displaced according to the equation:



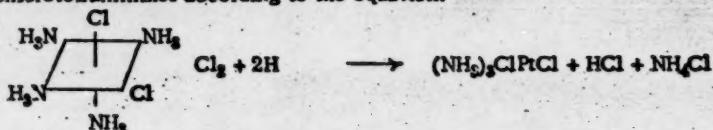
The trans-diammine, as will be seen from the equation:



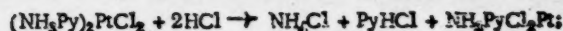
unfrees with pyridine, giving a triammine. In this case, again, the reactions lead to compounds of completely different types. It is remarkable that the same sort of thing occurs also with quadrivalent platinum—and not only in replacement reactions, but also in reductions to the bivalent state. Thus, trans-dichlorotetrammines are reduced according to the equation:



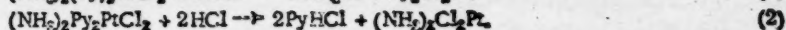
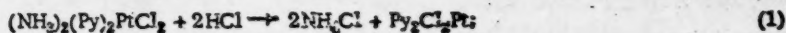
and cis-dichlorotetrammines according to the equation:



As will be seen from these equations, in the first case bivalent platinum tetrammines are formed, and in the second case triammines. We again observe different types of reactions depending on the geometric structure of the inner sphere. We will cite one further example of the difference in the reactions of isomers. This example was discovered much earlier than the preceding ones by Jørgensen, who found, when studying the effect of hydrochloric acid on isomeric tetrammines, that cis-tetrammines give only one product in this reaction—a mixed trans-diammine according to the equation:



whereas trans-tetrammines give two compounds differing in composition, according to the equations:



The examples that I have quoted are not isolated ones, but are typical for whole classes of compounds having identical geometrical structure, but different build-up, and are therefore, characteristic not of the molecule or ion entering into reaction, but of the inner sphere of the reacting complex compound. This means that a knowledge of this difference may enable a more precise picture of the chemical structure of the inner sphere to be obtained. Also, the difference in the reactions is not confined to their results, but it is found that the reaction process itself often shows a difference that is not less than the difference in the composition of the product. It is remarkable that this considerable difference in the chemical behavior of isomers was originally interpreted as a consequence of their differences in chemical structure, which was then assumed to be exactly like that of carbon compounds.

As soon as Werner's coordination theory was established, there arose a tendency to supplement the description in terms of this theory of the properties of geometric isomers by reactivity factors, using, in one way or another, the methods developed from structural theory as applied in organic chemistry. The reason for this tendency was the conviction that such fundamental differences in chemical behavior could not be explained in terms of only spatial differences in the disposition of atoms in geometric isomers.

It would be on the whole superfluous to give an exposition of the attempts that have been made to apply structural concepts that are completely incompatible with the possibility of geometric isomerism, but the ideas of Kurnakov, which are of interest in this respect, may be cited. Kurnakov considered that geometric isomerism is possibly associated with the structural method by which the bond halogen-nitrogen (which coexists with the bond halogen-metal) is formed. Schematically, the state of halogen in cis compounds will be represented from this point of view as N-Cl-Pt, and in trans compounds as N-Cl-Pt. Kurnakov came to this conclusion on the basis of investigations of the physical properties of complex compounds. However, chemical properties, which indicate a weakening of bonds in trans compounds, are in conflict with this suggestion, for formation of bonds with two nitrogens in trans compounds is bound to strengthen the platinum-chlorine bond. Also, the possibility of indicating the increase in mobility of halogens placed trans to one another by a change in the structural formulas, or, more accurately, by a special disposition of valency units, is rather remote. This will be clear from the following considerations: with continuous change in temperature or solvent properties, the mobility of the halogens will also change continuously, though it is obvious that it is quite impossible to make these changes continuously by means of any change in the separate valency units.

If Kurnakov's point of view were correct, then the difference in properties between geometric isomers would depend not only on the spatial arrangement of the constituent atoms, but also on the difference in the compositions of the inner spheres of the atoms united to the central atom. It is clear that for the chlorides found in cis and in trans positions, the compositions of the inner spheres are quite different: in one case two nitrogens

and platinum are to be found in the inner sphere, and in the other case one nitrogen, a chlorine, and a platinum are to be found. Thus, there is a difference even in type of compound. Hence, the possibility of the direct action of inner-sphere substituents on one another must be excluded, for this direct action finds expression as the presence of a valency bond, if it is translated into the language of the theory of structure.

However, the limitation of the number of valency units remains true for the chemistry of complex compounds. Hence, if the correctness of the theory of structure is accepted, then the question of the mutual influence of atoms not directly united to one another must be discussed in terms other than valency units, which are fitted for the expression of the changes of atoms that are directly united together. If, therefore, we wish to express in some way or other the mutual influence of two chlorines in ammonium chloroplatinate or of two hydrogens in hydrocarbons, then for the representation of this process we must always introduce the central atom as a transmitter of this influence. In other words, if it is necessary to express (formally) in some way the interaction of two atoms, then the results of an examination of a three-body problem must be brought to bear on the question. That is to say, the problem of expressing mutual influence in the simplest possible case is as much more complex than the problem of a bond as the three-body problem is more complex than the two-body problem. Consequently, there is nothing surprising and nothing that is contrary to the principles of the theory of structure in the fact that the mutual influence is effected through the central atom.

This mutual influence, when it is assumed to be transmitted only in the trans direction, is fully sufficient to explain the difference, of which I have given examples above, in the chemical behavior of geometric isomers. In addition to its direction, this mutual influence must be ascribed also a definite sense, revealed as a weakening of the trans bond or, what amounts to the same, an increase in the mobility of the trans substituent, whatever its chemical character may be. This "trans effect" does not preclude the possibility of a cis effect, but only under one condition, namely that the "cis effect" also, which naturally has the opposite sign to that of the trans effect (i.e., reduces the mobility of the inner-sphere substituents), shall be effected through the central atom. I shall not cite further examples of the manifestation of the trans effect in the substitution reactions of complex platinum compounds: In a recent article I published a collection of such examples in connection with a discussion on the trans-effect principle. Also, I shall not consider cases of reactions with complex compounds that are not entirely explicable from the point of view of the trans effect: these also were enumerated in the same article; they are few, and they have not yet been fully investigated. In any case, the trans effect can form the basis of further investigations in the chemistry of complex compounds, and for this reason the theoretical basis of this phenomenon and the determination of the extent to which it may be applied to elements other than platinum are of considerable interest.

It is most probable that it results from certain very general properties of the atom that are not yet amenable to precise investigation. The attempt to express the trans effect as a consequence of resonance structures, as Syrkin did, must be rejected. Syrkin was unable to extend his "explanation" to quadrivalent platinum and other elements having an octahedral configuration. For this same reason the American reviewers Quagliano and Schubert also confined their treatment to bivalent platinum, i.e., did not give a full treatment of the subject. Nevertheless, in the chemistry of quadrivalent platinum and cobalt the trans effect is manifested no less clearly than in that of bivalent platinum, i.e., the octahedral configuration is in this respect in no way different in principle from the square configuration; conclusions drawn from the trans-effect principle for quadrivalent platinum are, as a rule, borne out in practice.

One of the problems in the investigation of complex compounds is the provision experimentally of examples of geometric isomerism for as many as possible of the elements that give complex compounds. It is probable that the absence, in the case of many of the elements, of the geometric isomers predicted by theory, results simply from insufficient study of the chemistry of these elements and from the primitive methods of synthesis so far applied in inorganic chemistry. Another general problem relating to the trans effect is to find an approach to the explanation of the small difference in physical properties between isomers when considered in relation to the enormous difference in their chemical behavior, a fact that is in conflict with normal electrostatic concepts. We have the paradoxical position, that the cause of the increased reaction rate in the trans position is a more powerful factor than the electric field in the molecule, but that the trans effect, as it is manifest in a nonreacting molecule, has, for some reason or other, an extremely feeble effect on the physical properties of the molecule. Even the fact that the trans effect of the molecule in the solid is insignificantly small is of fundamental importance, for, as it is absent, we may regard the trans effect as something that arises in the very moment of reaction in the inner sphere and is nonexistent in the resting molecule.

Investigations carried out under the influence of the idea of the trans effect have been based on the

assumption that this phenomenon is elementary in character, i.e., it has been assumed that, for example, the order of substituents according to the magnitudes of their trans effects is independent of the nature of the central atom, is independent also of the chemical function of the substituent that is entering the inner sphere, and is still less dependent of the cis addend. Actually, however, no one has really analyzed the position in order to discover to what extent the circumstances that I have enumerated give evidence of the elementary nature of the inner-sphere reactions in which the trans effect is manifest.

A systematic investigation should be undertaken of the behavior of complex compounds formed by various central atoms in various solvents, in order to elucidate the effect of the medium on the trans effect. It is known that the chemical nature of the solvent can change reaction rate by a very high factor (Menshutkin). The question arises, whether this change in rate, which will probably occur also for complex compounds, will be different for cis and trans substitutions. Is it possible for a transition from trans laws to cis laws, or the formation of a mixture of geometric isomers, to take place only by changing the solvent? It has, in fact, been shown by experiment, that the formation of a definite geometric isomer does not depend on the trans effect of the group entering the inner sphere, but only on the substituents already attached to the central atom. When this fact is taken into account, it is difficult to suppose that the solvent will play a determining role in geometric isomerism, but experiments in this direction are nevertheless very desirable.

There is a very real need for the discovery of unequivocal methods of determining the state of atoms in the molecule of a complex compound and for the determination of the nature of the bonds in the molecule. In the present state of the question it is in general impossible to design any experiments (having a chance of being successful) based on the concept of a definite type of bond, and at the same time the question of the selective character of the bonds in a complex compound is in need of solution. I have in view the discovery of some method, even an approximate one, of determining the strength of the bonds of the central atom with any substituent, the strength of the bond formed by this atom with oxygen, for example, being taken as a starting point. It is of interest that the trans effect gives a certain indication of the changes in the strengths of the bonds, but it is not a simple problem to derive absolute values of bond strengths from the trans effect. It is very possible that a solution of this problem may be approached by the discovery of a quantitative characterization of the trans effect expressed in arbitrary units.

In the present Five Year Plan, a fairly wide scheme of investigation is contemplated having as its aim the initiation of work on the quantitative determination of the magnitude of the trans effect. Apart from the obtaining of data on rates of substitution in the inner sphere, other methods of measuring the trans effect will be developed, mainly by the determination of the physical properties of geometric isomers. One of the most important methods suitable for exact measurement is that depending on the investigation of the crystal structures of complex compounds. It is probable that exact determinations of interatomic distances will enable the way in which the trans effect depends on interatomic distances to be found, although it is not altogether certain that such dependence exists. One of the most interesting directions for investigation lies in the determination of the effect of geometric isomerism on the arrangement of atoms in the crystal, for even a partial solution of this problem enables an approach to be made to the determination of the nature of the forces participating in the formation of structures consisting of molecules, not ions, and if a complete solution is found it will be possible to predict the crystal structures of all geometric isomers on the basis of a determination of the structure of one of them.

If the search for a quantitative characterization of the trans effect leads only to a perfection of methods of determining heats of reaction and of electrical and optical properties of complex molecules, to the discovery of some quantitative relations between changes in these properties and the structures of the compounds, and to nothing more than these, even then the trans effect will have acted as a stimulus to the further development of science. However, the further we go, the greater are the number of questions that arise in connection with the trans effect, and it seems to me that the problem of the trans effect will be solved completely only in the very distant future. In the near future, apart from the determination of the physical properties that I have enumerated, it is necessary to intensify work on the synthesis of complex compounds with a view to the investigation of new types of isomerism. The possibilities of synthesizing complex compounds of new types are still far from exhausted, and it must always be remembered that every synthesis of a new compound and proof of its structure constitutes not only the establishment of the fact of the existence of this compound, but, at the same time is a service to the further development of science.

N. S. Kurnakov Institute of General
and Inorganic Chemistry of the
U.S.S.R. Academy of Sciences

Received December 28, 1952

GEOMETRIC AND ENANTIOMORPHIC ISOMERISM OF THE TRIAMMINES $[\text{EnAmPtClBrNO}_2]\text{X}$

I

In previous work [1, 2] we have studied the geometric isomerism of a new type of cyclic triamine having three different acid groups in the inner sphere, the example taken being the compound $[\text{EnNH}_3\text{PtClBrNO}_2]\text{Cl}$. By making use of the trans-effect principle, we succeeded in preparing the first five of the six possible isomers of this compound. They were all found to be quite stable compounds, differing in chemical and physical properties.

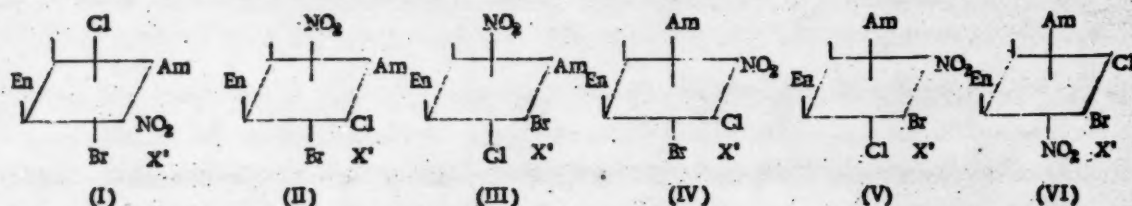


TABLE 1

Properties	 Isomer I	 Isomer II
Color	Pure yellow	Lemon yellow
Solubility at 25° (%)	45.14	27.30
Refractive indices	$n_D = 1.75-1.76$ $n_p = 1.714$	$n_D > 1.78$ $n_p = 1.76$
Action of alkalis	Forms soluble products (of hydrolysis ?)	Forms the crystalline amido compound $\text{EnCH}_2\text{NHCINO}_2\text{BrPt}$
Action of ammonia	Forms the cis-tetrammine $\text{EnCH}_2\text{NH}_2\text{NO}_2\text{NH}_3\text{BrPtCl}_2$	Reversible interaction
Action of nitrites	Forms the cis-dinitrotetrammine $\text{EnCH}_2\text{NH}_2\text{NO}_2 \cdot \text{NO}_2\text{BrPtCl}$	Reversible interaction

We decided to prove that for this type of compound, as for the previously studied dichloronitrotetrammines $[\text{EnAmPtCl}_2\text{NO}_2]\text{Cl}$ (where $\text{Am} = \text{NH}_3, \text{CH}_3\text{NH}_2, \text{C}_2\text{H}_5\text{NH}_2$) [3, 4, 5], change in the composition of the ammine part of the molecule should not effect the direction of inner-sphere replacement reactions. For this purpose we investigated the geometric isomerism of the methylamine

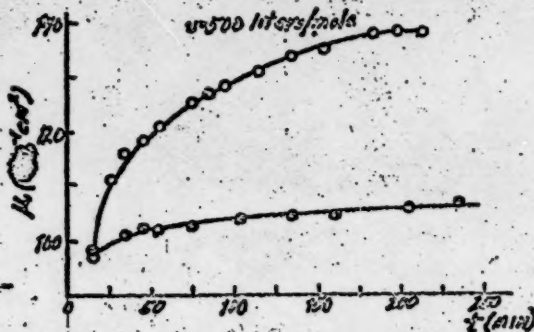
triammine $[\text{EnCH}_2\text{NH}_2\text{PtClBrNO}_2]\text{Cl}$. In the present communication we publish data on the synthesis of the first two isomers, and these fully confirm the correctness of the supposition we have expressed. Both compounds were prepared by procedures similar to those used in the synthesis of the ammonia compounds. Investigations of their properties showed that replacement of ammonia by methylamine has no appreciable effect on chemical properties. A comparison of the properties of the isomers is made in Table 1 and in the Figure.

While studying the geometric isomerism of the ammonia and methylamine triammines $[\text{EnAmPtClBrNO}_2]\text{Cl}$, we also attempted a comparative investigation of their optical activity. An interesting peculiarity of this type of compound is that all six possible geometric isomers should also possess enantiomorphs. In a number of investigations, begun by Chernyaev and continued by him in conjunction with Litvak, of the triammines $[\text{EnAmPtCl}_2\text{NO}_2]\text{Cl}$, where $\text{Am} = \text{NH}_3, \text{CH}_3\text{NH}_2, \text{Py}$ [6, 7], and $[\text{EnAmPtCl}_2(\text{NO}_2)_2]$ [4, 7], it was shown that geometric isomerism and the composition of the ammine part of the molecule have appreciable effects on the sign of rotation and on the coefficient of amido-inversion. Change in the composition of the acid substituents also has an appreciable effect on the rotation coefficients. It was of interest to observe the effect of the introduction of bromine on the optical activity constants of the compound.

Unfortunately, all attempts to separate either the ammonia or the methylamine triammines of structure I

Molecular conductivity of isomeric triammines:

— Isomer I
— Isomer II



The results of our determinations of specific and molecular rotation, dispersion coefficient, and amido-inversion coefficient for these compounds are given in Table 2, and for comparison data for the corresponding dichloronitrotriammines are given also. Dispersion coefficients α_D/α_C had to be replaced by the ratio α_E/α_C in all cases, because the salts under investigation were colored and measurement of α_D for them was rendered very difficult on account of absorption.

The feature that is immediately evident on comparing our results is the identical sign (+) of the difficultly soluble combinations $\text{EnNH}_2\text{ClNO}_2\text{BrPtCl}_2\text{H}_2\text{O}_3$ and $\text{EnCH}_2\text{NH}_2\text{ClNO}_2\text{BrPtCl}_2\text{H}_2\text{O}_3$. In the case of the dichloronitrotriammines $\text{EnNH}_2\text{Cl}_2\text{NO}_2\text{PtCl}$ and $\text{EnCH}_2\text{NH}_2\text{Cl}_2\text{NO}_2\text{PtCl}$, on the other hand, replacement of ammonia by methylamine leads to change in the sign of rotation, although the solubilities of the hydrogen tartrates of the dextro and levo enantiomorphs are considerably closer for the methylamine triammine than for the ammonia triammine [1, 3]. It is evident that when bromine is introduced the relation between the solubilities of the diastereoisomeric forms changes further, proceeding as far as a change in sign of the difficultly soluble combination. It would be interesting to verify whether the same picture is to be observed when these compounds are crystallized out as salts of other active acids.

The introduction of bromine results in a considerable approach in the amido-inversion coefficients of the two triammines (they are practically equal: $\rho \sim 5-6$), whereas for the dichloronitrotriammines this coefficient increases 5-7 times on going from the ammonia to the methylamine compound ($\rho_1 \sim 4$; $\rho_2 \sim 21-29$).

The rotatory power of the methylamine triammines is less than that of the ammonia triammines. In the case of the ammonia triammines, replacement of one chlorine by bromine results in a rotatable reduction in the rotation ($[\text{M}]_D^{25} = 40^\circ$; $[\text{M}]_D^{25} = 14^\circ$). The coefficient ρ rises somewhat at the same time. The dispersion also increases, owing to the brighter color of $\text{EnNH}_2\text{ClNO}_2\text{BrPtCl}$ in comparison with $\text{EnNH}_2\text{ClNO}_2\text{ClPtCl}$.

In the case of the methylamine triammines it is impossible to form an opinion concerning the relation between the rotatory powers, for $\text{EnCH}_2\text{NH}_2\text{ClNO}_2\text{ClPtCl}$ was not cleanly separated into its enantiomorphs and it was not found possible to isolate the second (levo) enantiomorph of $\text{EnCH}_2\text{NH}_2\text{ClNO}_2\text{BrPtCl}$. Nevertheless, the agreement between results for the dextro enantiomorphs obtained in parallel experiments ($[\text{M}]_D^{25} = 8.68-9.05$) gives reason to believe that it was isolated in an adequately pure form. The lowering of the dispersion coefficient for the dextro enantiomorph in comparison with that of the ammonia compound may be explained by the fact that the measurements were carried out on the nitrate, which is somewhat lighter in color than the chloride.

Thus, the introduction of bromine into the dichloronitrotriammine molecule has an appreciable effect on the rotatory power and on the relation between the ρ coefficients and the signs of the more difficultly soluble combinations for the ammonia and methylamine triammines.

EXPERIMENTAL

I. Synthesis of $\text{EnCH}_2\text{NH}_2\text{NO}_2\text{ClBrPtCl}$ (Isomer I)

We synthesized Isomer I following the method used for the corresponding ammonia compound [1], the

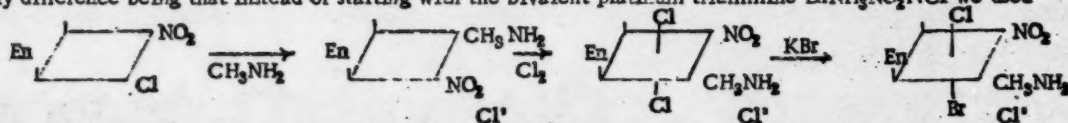
into their enantiomorphs in the form of hydrogen d-tartrates, d-camphorsulfonates, and α -bromo-d-camphorsulfonates did not give positive results. The solubilities of the diastereoisomeric forms are evidently very close together. The corresponding triammines of the dichloronitro series $\text{EnAmNO}_2\text{Cl}_2\text{PtCl}$ do not possess enantiomorphs.

We succeeded in separating isomers of structure II, $\text{EnNH}_2\text{ClNO}_2\text{BrPtCl}$ and $\text{EnCH}_2\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ into their enantiomorphs in the form of hydrogen d-tartrates.

TABLE 2

Compound	Sign of the difficultly soluble com- bination	$[\alpha]_D$	$[M]_D$	α_E/α_C	ρ
1. $\text{EnNH}_3\text{ClNO}_2\text{ClPtC}_4\text{H}_9\text{O}_6$ $\underline{\text{d-EnNH}_3\text{ClNO}_2\text{ClPtCl}}$ $\underline{\text{l-EnNH}_3\text{ClNO}_2\text{ClPtCl}}$	[6] (++)	+ 9.55 - 2.5	+ 40.54 - 10.0	+ 1.79 2.00	+ 4.23 3.68
2. $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{ClPtC}_4\text{H}_9\text{O}_6$ $\underline{\text{l-EnCH}_3\text{NH}_2\text{ClNO}_2\text{ClPtCl}}$ $\underline{\text{d-EnCH}_3\text{NH}_2\text{ClNO}_2\text{ClPtCl}}$	[4] (++)	- 1.86 + 0.67	- 8.16 + 3.06	2.14 2.16	29.5 20.79
3. $\text{EnNH}_3\text{ClNO}_2\text{BrPtC}_4\text{H}_9\text{O}_6$ $\underline{\text{d-EnNH}_3\text{ClNO}_2\text{BrPtCl}}$ $\underline{\text{l-EnNH}_3\text{ClNO}_2\text{BrPtCl}}$	(++)	3.02 - 2.81	14.16 - 13.18	2.10 2.22	5.83 5.92
4. $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtC}_4\text{H}_9\text{O}_6$ $\underline{\text{d-EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtNO}_2}$	(++)	1.70 1.78	8.68 9.05	1.50 1.30	5.09 4.99

only difference being that instead of starting with the bivalent platinum triammine $\text{EnNH}_3\text{NO}_2\text{PtCl}$ we used



the corresponding methylamine compound. The intermediates required were prepared by the method previously described [4].

The labile place in the molecule $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{Cl}_2\text{PtCl}$ is the coordinate Cl-Cl . One of the chlorines of this compound may be readily replaced by ammonia with formation of the cis-tetrammine $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{-NH}_3\text{ClPtCl}_2$, and by the NO_2 group with formation of the cis-dinitro compound $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{NO}_2\text{ClPtCl}$; in a similar way by the action of the theoretical amount of potassium bromide, one atom of chlorine is replaced by bromine with the formation of a compound corresponding in composition and structure to isomer I. The reaction proceeds when the reaction mixture is heated on a water bath for one-two hours and then evaporated until crystallization begins. The compound is a pure-yellow substance and crystallizes without water.

Found %: Pt 40.63; 40.62; 40.23; Br 16.55; Cl 15.86.

$\text{EnCH}_3\text{NH}_2\text{NO}_2\text{ClBrPtCl}$. Calculated %: Pt 40.40; Br 16.56; Cl 14.67.

In full accord with the configuration of isomer I, the compound that we prepared readily reacts with replacement of the chlorine, which is labilized by the trans-active bromine. By the action of ammonia in theoretical quantity or in excess, the cis-tetrammine $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{NH}_3\text{BrPtCl}_2$ was obtained. Only chlorine occurs in the inner sphere of this compound, a fact shown by potentiometric titration of the outer-sphere halogen. Consequently, the bromine is in the inner sphere and the original triammine is indeed compound I and not its isomerization isomer $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{Cl}_2\text{PtBr}$.

Found %: Pt 39.51; Br 15.12; Cl 15.21; Cl_{ion} 13.92.

$\text{EnCH}_3\text{NH}_2\text{NO}_2\text{NH}_3\text{BrPtCl}_2$. Calculated %: Pt 39.02; Br 15.97; Cl_{ion} 14.17.

The inner-sphere chlorine is readily replaced also by a nitro group. When a cold, slightly alkaline concentrated solution of $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{ClBrPtCl}$ is treated with sodium nitrite, the reaction mixture becomes appreciably lighter in color and after a time a lemon-yellow substance begins to separate; it corresponds in composition to a cis-dinitro compound.

Found %: Pt 39.27; 39.55; 39.36; Br 16.07; Cl 7.73

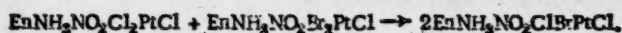
$\text{EnCH}_3\text{NH}_2\text{NO}_2\text{NO}_2\text{BrPtCl}$. Calculated %: Pt 39.54; Br 16.18; Cl 7.17

It is possible, without isolating the chloride, to isolate the amido compound $\text{EnCH}_3\text{NHNO}_2\text{NO}_2\text{BrPt}$, by treating the reaction mixture with excess of alkali. The amido compound is a bright-orange substance that crystallizes well.

Found %: Pt 42.96; 42.85.
 $\text{EnCH}_3\text{NHNO}_2\text{NO}_2\text{BrPtCl}$. Calculated %: Pt 42.69.

In the same way as compounds of similar structure, the dichloronitrotriamines $\text{EnAmNO}_2\text{Cl}_2\text{PtCl}$ ($\text{Am}=\text{NH}_2$ and CH_3NH_2) and the ammonia bromochloronitrotriamine $\text{EnNH}_2\text{NO}_2\text{ClBrPtCl}$, the compound that we have prepared does not give an amido compound on treatment with alkalis: its solution in caustic alkali takes up a bright color that gradually grows darker.

It was shown for the ammonia triamine $\text{EnNH}_2\text{NO}_2\text{ClBrPtCl}$, that the formation by the action of potassium bromide on $\text{EnNH}_2\text{NO}_2\text{Cl}_2\text{PtCl}$ of this bromochloro compound instead of a mixture of dichloro and dibromo derivatives is to be attributed to the double-decomposition reaction that occurs between these compounds:



This is equally true also for the methylamine triamine $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{ClBrPtCl}$.

The trans-dibromo derivative $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{Br}_2\text{PtCl}$ was prepared by the oxidation of $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{PtCl}$ by bromine.

Found %: Pt 36.52; 36.63; Br 31.02; Cl 6.40.
 $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{Br}_2\text{PtCl}$. Calculated %: Pt 36.99; Br 30.28; Cl 6.71

When an equimolecular mixture of this compound and $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{Cl}_2\text{PtCl}$ is heated, there separates from solution not a mixture of crystals of the original compound, but a chemical compound of composition and properties corresponding to isomer I.

Found %: Pt 40.44
 $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{ClBrPtCl}$. Calculated %: Pt 40.40

Refractive-index measurements on samples of the salt obtained by the two methods gave agreeing results: $n_D = 1.75-1.76$; $n_D = 1.714$; extinction angle 45° .

Determination of the electrical conductivity of isomer I indicates that the compound forms two ions and undergoes far-reaching hydrolysis in the course of time.

On dilution ($t = 25^\circ$)

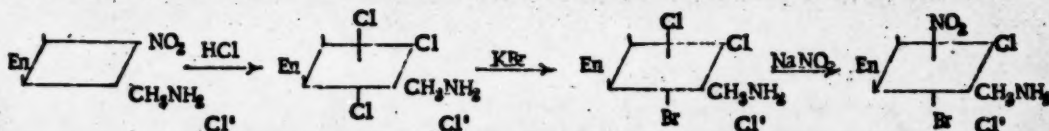
V	1000	2000	4000 liter/mole
μ	103.5	104.7	107.3 $\Omega^{-1}\text{cm}^2$

On reaction with water:

t (min)	$\mu (\Omega^{-1}\text{cm}^2)$	t (min)	$\mu (\Omega^{-1}\text{cm}^2)$
15	98.6	85	127.2
25	111.5	95	128.3
35	115.8	115	131.4
45	118.3	135	133.7
55	121.3	155	135.2
65	123.1	185	137.9
75	125.5	215	137.9
		245	140.9

II. Synthesis of $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ (Isomer II)

Trans-effect theory indicated a method of synthesis for isomer II similar to that used for the corresponding ammonia compound (I), namely:



The triamines $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{PtCl}$ and $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$ have been described previously [4] and we

prepared them by the methods given. It should be mentioned, however, that the first fractions of $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$ isolated from hydrochloric acid solution generally had a considerably elevated (by 5-6%) platinum content. Crystal-optical investigation of the product showed that it contained two phases, which could be separated by repeated crystallization. The admixed material was isolated as a white salt of composition $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$.

Found %: Pt 54.72; Cl 20.11
 $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$. Calculated %: Pt 54.64; Cl 19.84.

It is evident that HCl reacts with $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{PtCl}$ with complete destruction of the nitro group and formation of $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$. The chlorine liberated when the nitro group is destroyed does not completely oxidize $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$. Chlorination of the fraction of platinum content 50.66% led to the formation of the almost pure salt:

Found %: Pt 45.11
 $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$. Calculated %: Pt 45.49.

In order to control the purity of $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$ the refractive indices of this compound and of the corresponding triammine of bivalent platinum were determined.

$\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$

$n_D = 1.76$

$n_p = 1.712$

$n_m = 1.734$

$\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$

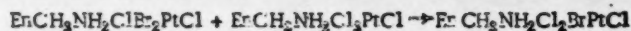
$n_D = 1.685$

$n_p = 1.596$

$n_m = 1.664$

It was essential for the performance of the next stage of synthesis - replacement of one of the chlorines on the coordinate Cl-Pt-Cl by bromine - that $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$ should be particularly pure. Otherwise side reactions would occur leading to formation of green compounds that greatly hinder the isolation of pure $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{BrPtCl}$. The same difficulty, though in appreciably lower degree, is met when the ammonia triammine $\text{EnNH}_3\text{Cl}_2\text{PtCl}$ is caused to react with potassium bromide.

The stereochemical reaction resulting in the formation of $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{BrPtCl}$ is analogous to the replacement of one chlorine by bromine in $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{Cl}_2\text{PtCl}$. It is evident that here also the trans-dibromo compound formed, $\text{EnCH}_3\text{NH}_2\text{ClBr}_2\text{PtCl}$, reacts with unchanged $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{PtCl}$ molecules according to the equation:



Found %: Pt 41.02; 41.10; 41.21; Br 16.71; 16.42; Cl 23.05; 22.79.

$\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{BrPtCl}$. Calc. %: Pt 41.30;

Br 16.90

Cl 22.50.

The most mobile chlorine in the molecule $\text{EnCH}_3\text{NH}_2\text{Cl}_2\text{BrPtCl}$ must be that situated on the same coordinate as the bromine. Treatment with a concentrated, slightly alkaline, cold solution of the calculated amount of sodium nitrite is followed fairly rapidly by the separation of a compound of composition corresponding fairly closely to $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$.

Found %: Pt 39.40, 40.12, Br 18.36, Cl 13.60, Cl_{ion} 7.20, 7.04

$\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$. Calc. %: Pt 40.40, Br 16.56, Cl 14.67, Cl_{ion} 7.33

This triammine differs sharply in its properties from that of the same composition, but of configuration I; it is very similar to its ammonia analog $\text{EnNH}_3\text{ClNO}_2\text{BrPtCl}$; it is less soluble in water and is lighter in color than isomer I. Under the action of alkali, a proton readily splits from the methylamine group, yielding the amidodiamine $\text{EnCH}_3\text{NHCINO}_2\text{BrPt}$:

Found %: Pt 43.76, 44.10; Br 16.35; Cl 7.59; Br: Cl = 1:1.04.

$\text{EnCH}_3\text{NHCINO}_2\text{BrPt}$. Calculated %: Pt 43.69;

Br 17.88; Cl 7.93.

Treatment of this with hydrochloric acid yields pure isomer II:

Found %: Pt 40.36; Br 16.80; Cl 14.40

Reprecipitation of the amido compound by addition of alkali to its solution in hydrochloric acid does not always lead to purification of the compound. Generally, the platinum content of the salt rises owing to partial splitting off of inner-sphere bromine in the alkaline medium and its replacement by chlorine.

Found %: Pt 45.41, 45.84; Br 8.64, 9.23; Cl 12.26, 11.96

$\text{EnCH}_3\text{NHCINO}_2\text{BrPt}$. Calculated %: Pt 43.69, Br 17.88, Cl 7.93

Because of these facts the reprecipitation of the amido compound in the experiments designed to separate the compound into its enantiomorphs was carried out from nitric acid solutions and the rotation was measured for the nitrate of the triammine.

Isomer II, unlike isomer I, slowly dissolves when treated with ammonia solution, but it was not found possible to isolate a tetrammine: the original salt remained in the solid phase. Also, it does not react with sodium nitrite, which is probably to be explained, as in the case of other triammines having an $\text{NO}_2\text{-Pt-X}$ coordinate, by the ready reversibility of replacement reactions involving halogens standing opposite to the strongly trans-influencing nitro group.

Thus, the chemical properties of the triammine obtained, $[\text{EnCH}_2\text{NH}_2\text{PtClBrNO}_2]\text{Cl}$ corresponds to the configuration of isomer II, as it should do according to the method by which it was prepared. Refractive-index determinations gave the following results: $n_D^{25} > 1.78$; $n_D^{25} = 1.76$. Conductivity determinations showed that this compound of configuration I is only slowly hydrolyzed.

On dilution ($t = 25^\circ$)

$V = 500 \quad 1000 \quad 2000 \quad 4000 \text{ liter/mole}$

$\mu = 97.5 \quad 100.5 \quad 100.5 \quad 100.0 \Omega^{-1}\text{cm}^2$

On reaction with water:

$t \text{ (min)}$	$\mu, \Omega^{-1}\text{cm}^2$	$t \text{ (min)}$	$\mu, \Omega^{-1}\text{cm}^2$
25	98.1	105	104.3
35	100.9	135	104.3
45	101.3	165	104.7
55	102.1	205	105.9
75	102.7	235	106.7

III. Separation of $\text{EnNH}_2\text{ClNO}_2\text{BrPtCl}$ into its Enantiomorphs

The separation was effected by crystallization of the triammine in the form of its hydrogen tartrate. The theoretically calculated amount (2.322 g) of $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ was added to a solution of $\text{EnCH}_2\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ (6 g) in water (146 ml), AgCl was separated, and the amount of tartaric acid calculated for the formation of the hydrogen tartrate (0.95 g) was added. The salt began to crystallize after two weeks, when the solution attained a concentration of 20% with respect to the triammine hydrogen tartrate.

Fraction I of the crystals (2.1 g) was a light yellow, finely crystalline substance of low solubility in cold water. The configuration of the less soluble combination was (+).

Found %: Pt 32.86

$\text{EnNH}_2\text{ClNO}_2\text{BrPtC}_4\text{H}_4\text{O}_6$ Calculated %: Pt 33.51.

The hydrogen tartrate was dissolved in a 1% solution of HCl and then treated with an excess of alkali. The amido compound that separated was filtered off, washed with cold water, and reprecipitated from hydrochloric acid solution.

Found %: Pt 44.86, 44.91.

$\text{EnNH}_2\text{ClNO}_2\text{BrPt}$.

Calculated %: Pt 45.13.

After the second precipitation of the amido compound, the filtrate showed no rotation.

Determination of the Rotation of $d\text{-EnNH}_2\text{ClNO}_2\text{BrPtCl}$ (Fraction I).

Weight of amido compound 0.2227 g; $V = 13 \text{ ml H}_2\text{O}$ containing an excess of HCl ; $l = 1.5 \text{ dm}$; $c_{\text{chloride}} = 1.85$; $a_C = +0.05^\circ$; $a_D = +0.08^\circ$; $a_E = +0.11^\circ$; a_F —this could not be determined owing to the high light absorption.

$$a_E/a_C = 2.20; [a]_D = +2.92^\circ; [M]_D = +13.69^\circ.$$

It was not found possible to measure the rotation of the amido compound at this concentration: it separated out into the solid phase. We therefore had recourse to further dilution: 5 ml of the solution of the chloride ($c = 1.85$) was brought in alkaline solution up to a volume of 13 ml.

Determination of the Rotation of $l\text{-EnNH}_2\text{ClNO}_2\text{BrPt}$ (Fraction I).

$c = 0.57$, $l = 1.5 \text{ dm}$; $a_C = -0.06^\circ$; $a_D = -0.10^\circ$, $a_E = -0.13^\circ$.

$$a_E/a_C = 2.16; [a]_D = -11.69^\circ; [M]_D = -50.56^\circ; \rho = 3.69.$$

Fairly rapid racemization occurs in alkaline solution: the rotation was reduced to nil by the next day.

Fraction II of the crystals (0.56 g) was filtered off three days after the separation of Fraction I. In platinum content it corresponded to the normal tartrate crystallizing with one-half a molecule of tartaric acid.

Found %: Pt 35.96; 36.07.

$(\text{EnNH}_2\text{ClNO}_2\text{BrPt})_2\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{C}_4\text{H}_4\text{O}_6$ Calculated %: Pt 35.81.

The amido compound precipitated from this portion of the tartrate appeared to be pure and, in view of the small amount, was not reprecipitated. Pt found: 45.28%. Its chloride gave dextro rotation equal to that of the chloride of Fraction I.

Determination of the Rotation of d-EnNH₂ClNO₂BrPtCl (Figure II).

Amido compound, 0.3059 g; V = 17.50 ml H₂O containing 0.24 ml HCl (1:3); c = 1.89; \bar{l} = 2.4; $\alpha_C = +0.10^\circ$; $\alpha_D = +0.14^\circ$; $\alpha_E = +0.21^\circ$.

$$\alpha_E / \alpha_C = 2.10; [\alpha]_D = +3.02^\circ; [M]_D = +14.15^\circ.$$

Determination of the rotation of l-EnNH₂ClNO₂BrPt (Fraction II).

Caustic soda (10%, 0.27 ml) was added to the solution of the chloride; \bar{l} = 2.4 dm; c = 1.71; $\alpha_C = 0.53^\circ$; $\alpha_D = -0.80^\circ$; $\alpha_E = -1.07^\circ$; $\alpha_E / \alpha_C = 2.02$; $[\alpha]_D = -19.09^\circ$; $[M]_D = -82.58^\circ$; $p = 5.83$.

The agreement between the results of the rotation determinations for chloride from the two fractions of configuration (++) may be considered to be within the limits of experimental error. The divergence in the values of $[M]_D$ for the amido compound is to be explained by the inactivation of the compound in an alkaline medium, which proceeded to an appreciable extent during the dilution operation carried out on the solution of the amido compound of Fraction I.

The first two fractions comprised about one-third of the ammine hydrogen tartrate that could be formed from the chloride. Fraction III was filtered off two days after Fraction II (1.5 g). We did not succeed in measuring the rotation of the chloride, the angles being so small. However, the amido compound showed a definite levo rotation. From the mother liquor, after separation of Fraction III, the amido compound of Fraction IV (1.2 g) was separated by the action of alkali.

Found %: Pt 44.98.

EnNH₂ClNO₂BrPt. Calculated %: Pt 45.13.

For fear that it might undergo rapid racemization in alkaline solution, the amido compound was not reprecipitated: it was converted by the action of a small excess of hydrochloric acid into the chloride. Part of the chloride separated immediately from the solution (Fraction IVa), and a second fraction was separated after two days (Fraction IVb).

Found %: Pt 41.82, 41.44.

EnNH₂ClNO₂BrPtCl. Calculated %: Pt 41.62.

Both chloride fractions showed levo rotation.

Determination of the Rotation of l-EnNH₂ClNO₂BrPtCl (Fraction IVa).

Chloride, 0.4625 g; V = 13 ml; c = 3.55; \bar{l} = 1.5 dm; $\alpha_C = -0.09^\circ$; $\alpha_D = -0.15^\circ$; $\alpha_E = -0.20^\circ$; $\alpha_E / \alpha_C = 2.22$; $[\alpha]_D = -2.81^\circ$; $[M]_D = -13.18^\circ$.

The molecular rotation of the levo enantiomorph was 93% of the rotation of the dextro enantiomorph, which indicates an adequate completeness of separation.

Addition of alkali to a solution of the chloride (c = 3.55) caused reversal of the sign of the rotation, but it was not possible to measure the rotation owing to the precipitation of the amido compound. The measurement was carried out with amido compound at a twofold dilution.

Determination of the Rotation of d-EnNH₂ClNO₂BrPt (Fraction IVa).

\bar{l} = 1.5 dm; c = 1.63; $\alpha_C = +0.25^\circ$; $\alpha_D = +0.37^\circ$; $\alpha_E = +0.50^\circ$; $\alpha_E / \alpha_C = 2.00$; $[\alpha]_D = +13.90^\circ$; $[M]_D = +56.61^\circ$; $p = 4.29$. After acidification with hydrochloric acid, the solution lost its activity completely after two days; $[\alpha]_D = -0.37^\circ$; $[M]_D = -1.73^\circ$, consequently the process of inactivation proceeds also in acid medium, although more slowly than in alkaline.

Determination of the Rotation of l-EnNH₂ClNO₂BrPtCl (Fraction IVb).

Chloride, 0.1624 g; V = 13.0 ml; \bar{l} = 1.5 dm; c = 1.25; $\alpha_C = -0.03^\circ$; $\alpha_D = -0.04^\circ$; $\alpha_E = -0.06^\circ$; $\alpha_F = -0.11^\circ$; $\alpha_E / \alpha_C = 2.00$; $\alpha_F / \alpha_C = 3.66$; $[\alpha]_D = -2.13^\circ$; $[M]_D = -9.99^\circ$.

Determination of the Rotation of d-EnNH₂ClNO₂BrPt (Fraction IVb) (without further dilution).

\bar{l} = 1.5 dm; V = 13.0 ml of chloride solution + 0.3 ml 10% KOH; c = 1.12; $\alpha_C = +0.17^\circ$; $\alpha_D = +0.23^\circ$; $\alpha_E = 0.34^\circ$; $\alpha_F \approx 0.63^\circ$; $\alpha_E / \alpha_C = 2.00$; $\alpha_F / \alpha_C = 3.70$; $[\alpha]_D = +1.37^\circ$; $[M]_D = +59.26^\circ$; $p = 5.92$.

The amido-inversion coefficient from Fraction IV agrees well with the value from Fraction II of the dextro enantiomorph, for which the measurement of the rotation of the amido compound was carried out rapidly without further dilution. Admixture of racemate to this fraction of chloride should not affect the optical-activity coefficients.

IV. Separation of $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ into its Enantiomorphs

The triammine was separated into its enantiomorphs by crystallization in the form of the ammine hydrogen tartrate.

Experiment No. 1. To a solution of the chloride (3.3556 g), $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ (1.2631 g) and tartaric acid (0.5208 g, amount calculated for formation of the hydrogen tartrate) were added. The solution had a concentration of 10-15% with respect to ammine hydrogen tartrate. After considerable evaporation of the solution, a first fraction of well-formed crystals (1.28 g) corresponding in composition to the hydrogen tartrate was obtained. The configuration of the difficultly soluble combination was (+).

Found %: Pt 32.30.

$\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtC}_4\text{H}_4\text{O}_6$ Calculated %: Pt 32.71.

From this fraction, a double reprecipitation from a 1% solution of nitric acid yielded the amido compound.

Found %: Pt 43.54.

$\text{EnCH}_3\text{NHCINO}_2\text{BrPt}$ Calculated %: Pt 43.69.

Measurement of the Rotation of d- $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtNO}_3$ (Fraction D). The amido compound (0.3232 g) was dissolved in water (13 ml) containing HNO_3 (1:3) (0.21 ml); $l = 2.3$ dm; $c = 2.04$; $\alpha_C = +0.08^\circ$; $\alpha_D = +0.08^\circ$; $\alpha_E = +0.12^\circ$; $\alpha_E/\alpha_C = 1.5$; $[\alpha]_D = +1.70^\circ$; $[M]_D = +8.68^\circ$.

An excess (2 ml) of 10% KOH was added to the solution of the nitrate.

Measurement of the rotation of l- $\text{EnCH}_3\text{NHCINO}_2\text{BrPt}$ (Fraction I).

$V = 20$ ml; $l = 1.5$; $c = 1.616$; $\alpha_C = -0.15^\circ$; $\alpha_D = -0.24^\circ$; $\alpha_E = -0.32^\circ$; $\alpha_E/\alpha_C = 2.13$; $[\alpha]_D = -9.90^\circ$; $[M]_D = -44.32^\circ$; $\rho = 5.09$. The rotation of the alkaline solution had disappeared by the next day.

Further evaporation of the mother liquor after separation of the Fraction I crystals of the hydrogen tartrate led to formation of a sticky mass. By repeated dissolution and evaporation it was found possible to separate one further fraction of crystals. The amido compound obtained from them showed a very feeble rotation in acid medium, which it was not found possible to measure, but a definite dextro rotation was observed in alkaline medium. When alkali was added to the mother liquor after separation of Fraction II, no amido compound separated. We therefore did not succeed in obtaining the second enantiomorph.

As the results of the first experiment were somewhat unexpected - the difficultly soluble combinations of the ammonia and the methylamine triammines had the same configuration - we carried out a repeat experiment on the separation of $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ in the form of its hydrogen tartrate.

Experiment No. 2. The amido compound $\text{EnCH}_3\text{NHCINO}_2\text{BrPt}$ (4.0157 g) was dissolved in water (70-80 ml) containing the calculated amount (1.3488 g) of tartaric acid. After six days well-formed light yellow crystals (1.9 g) of the hydrogen tartrate separated from the solution.

Found %: Pt 33.09.

$\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtC}_4\text{H}_4\text{O}_6$ Calculated %: Pt 32.71.

The amido compound was obtained from Fraction I of the hydrogen tartrate by double reprecipitation. Its solution in nitric acid showed dextro rotation, the value being in accord with the results of the first experiment.

Measurement of the Rotation of d- $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtNO}_3$ (Fraction D).

The amido compound (0.4631 g) was dissolved in water (18 ml) containing HNO_3 (1:3) (0.30 ml); $c = 2.92$; $l = 2.3$ dm; $\alpha_C = +0.10^\circ$; $\alpha_D = +0.12^\circ$; $\alpha_E = 0.13^\circ$; $\alpha_E/\alpha_C = 1.30$; $[\alpha]_D = +1.78^\circ$; $[M]_D = +9.05^\circ$.

By the action of alkali (0.1 ml of 10% KOH) the sign of rotation was reversed: $V = 19$ ml; $c = 2.43$; $l = 2.3$ dm; $\alpha_C = -0.27^\circ$; $\alpha_D = -0.30^\circ$; $\alpha_E = -0.53^\circ$; $\alpha_E/\alpha_C = 1.96$; $[\alpha]_D = -7.13^\circ$; $[M]_D = -32.01^\circ$; $\rho = 3.53$. Owing to the strong absorption of the solution, the measurements were repeated at $l = 1.5$ dm: $\alpha_C = -0.21^\circ$; $\alpha_D = -0.29^\circ$; $\alpha_E = -0.38^\circ$; $\alpha_E/\alpha_C = 1.80$; $[\alpha]_D = -7.92^\circ$; $[M]_D = -35.38^\circ$; $\rho = 3.20$.

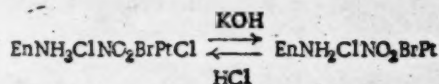
When an excess of alkali (2 ml) was added, the rotation coincided with the results for the rotation of the amido compound in Experiment No. 1: $V = 20$ ml; $c = 2.31$; $l = 1.5$ dm; $\alpha_C = -0.35^\circ$; $\alpha_D = -0.54^\circ$; $\alpha_E = -2.16^\circ$; $[\alpha]_D = -10.10^\circ$; $[M]_D = -45.22^\circ$; $\rho = 4.99$.

As in Experiment No. 1, it was not found possible to isolate the levo enantiomorph. However, the fairly good agreement between the absolute values of the rotation and coefficients of rotation for the dextro enantiomorph in the two experiments indicates that it is of high purity.

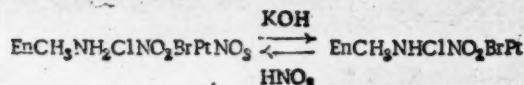
We take this opportunity of expressing our thanks to E.E. Burovaya and V. M. Ezuchevskaya for carrying out crystal-optical determinations and electrical-conductivity measurements on the compounds prepared.

SUMMARY

1. Two geometric isomers of the methylamine triammine of composition $[\text{EnCH}_3\text{NH}_2\text{PtClBrNO}_2]\text{Cl}$, and of structure $\text{EnCH}_3\text{NH}_2\text{NO}_2\text{ClBrPtCl}$ and $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ respectively have been prepared.
2. It has been shown that replacement of ammonia by methylamine in $[\text{EnAmPtClBrNO}_2]\text{Cl}$ does not have any appreciable effect on the course of the synthesis and on the chemical properties of the isomeric triammines.
3. Ammonia and methylamine triammines of identical structure - $\text{EnNH}_3\text{ClNO}_2\text{BrPtCl}$ and $\text{EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtCl}$ - have been separated into their enantiomorphs. Measurements have been made of the values of the rotations and dispersions of the compounds $d(l)\text{-EnNH}_3\text{ClNO}_2\text{BrPtCl}$ and $l(d)\text{-EnNH}_2\text{ClNO}_2\text{BrPt}$, $d\text{-EnCH}_3\text{NH}_2\text{ClNO}_2\text{BrPtNO}_2$ and $l\text{-EnCH}_3\text{NHCINO}_2\text{BrPt}$.
4. It has been shown that the configuration of the difficultly soluble combination for the two triammine hydrogen tartrates is identical ($++$), which is the reverse of the position found for the analogous dichloronitrotriammines.
5. It has been found that the amido-inversion coefficients ρ for the reactions



and



are very close in value, on the average about 6 for the first and about 5 for the second reaction; this behavior contrasts with that of the dichloronitrotriammines, for which ρ rises from 4-6 for the ammonia triammine to 21-29 for the methylamine triammine.

6. It has been shown that the rotatory power of the methylamine triammine is lower than that of the ammonia triammine.

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THERMOCHEMICAL INVESTIGATION OF ISOMERIC PLATINUM COMPOUNDS

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Thermochemical investigation of complex platinum compounds, particularly isomeric compounds, is capable of yielding material for the characterization of the energetics of the trans effect. A number of investigations has been devoted to the study of the isomeric changes of complex compounds of the platinum metals. Chugaev and Pshenitsyn [1] have established that the green salt $[\text{Pt}(\text{NH}_3)_2][\text{PtCl}_4]$, on being heated carefully at near the decomposition temperature, undergoes depolymerization to the trans monomer $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. In connection with this work it should be noted that as early as 1841 Fehling [2] showed that the salt $[\text{Pd}(\text{NH}_3)_2][\text{PdCl}_4]$, on being heated to 200°, underwent a similar change. An attempt to determine the difference in total energy between the cis and trans nitrites of platinum by estimating their heats of combustion in a calorimetric bomb, which was made in 1931 [3], was not successful; it was found that the heats of combustion of the cis and trans nitrites were identical, within the limits of experimental error.

Investigations into the thermal stability of complex compounds of platinum and the platinum metals, which were carried out by Grinberg, Pritsyn, Nikolaev, and Rubinshtein [4,5,6], showed that trans isomers are generally more stable than the corresponding cis isomers. Measurements [7] have shown that the specific heats of the cis- and trans-dichlorodiammineplatinums are identical between 20° and 50°.

The present work is devoted to the determination of the difference in total energy between the isomeric chloroammines of bivalent platinum on the basis of measurements of the heats of reaction of these isomers with aqueous ammonia.

It is known that the difficultly soluble isomeric chloroammines of bivalent platinum react on being heated with aqueous ammonia to 70-80° to give a solution of tetrammineplatinum (II) chloride, a compound that has no isomers. Hence the difference between the heats of reaction of the isomers with ammonia is a direct measure of the difference of the total energies of the isomers.

In choosing the method of investigation it was necessary to take the following points into account: 1) the difference between the total energies of the isomers is determined in the form of a small difference between two relatively large numbers - heats of reaction, which are directly measured; 2) the measurements of the heats of reaction have to be carried out at elevated temperatures (70-80°) in a volatile solvent; 3) the reactions studied may have a comparatively low rate; 4) it is desirable that it should be possible to work with small amounts of the salts.

EXPERIMENTAL

Apparatus and Method of Measurement

We constructed a hermetic calorimeter (for liquids) having constant heat exchange (adiabatic) and permitting the measurement of small amounts of heat for slow-running processes at temperatures ranging from room temperature to 100-120°. The calorimeter is in many ways similar to that constructed by Kiselev [8] for the measurements of heats of adsorption.

The general scheme of the arrangement is shown in the figure. (See plate, page 195). The calorimetric unit consists of the calorimeter 1, the liquid jacket 2, and arrangements for the regulation and measurement of temperature. The calorimeter itself, 1, consists of an inner thin-walled beaker, about 250 ml in volume, placed on a textolite stand in a thin-walled outer beaker, which is hermetically closed with a cover. The inner and outer beakers and the cover are made of stainless steel. The calorimeter is fixed in the center of the jacket by the aid of five tubes of stainless steel screwed into the cover of the outer beaker; through these pass the leads of the resistance thermometers, the axis of the stirrer, and an arrangement for breaking the ampoule containing the substance under investigation. The jacket 2 is a cylindrical vessel, volume about 30 liters, filled with a mixture (1:1) of transformer oil and kerosene. Stirring in the jacket is effected by means of a propeller stirrer situated in the tube 3.

The changes in temperature in the calorimeter are measured by a platinum resistance thermometer, resistance about 127 ohms at 70°, and a bridge. Two arms of the equal-arm Wheatstone bridge 4 consist of ten-ohm

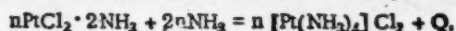
resistances; the thermometer in the calorimeter and a constant resistance of 127 ohms form the other two arms of the bridge. In parallel with the 127-ohm coil is a precision six-dialed resistance box, which serves for the maintenance of the balance of the bridge and allows measurements to be made of the change in resistance of the thermometer with change in temperature. A mirror galvanometer having a period of three seconds and a p.d. sensitivity of $1 \text{ mm/m} \approx 6 \cdot 10^{-8} \text{ V}$ is placed in the diagonal of the bridge. The equilibrium of the bridge is controlled by the aid of a viewing tube and scale, which is placed at a distance of six meters from the galvanometer. The arrangement described permits a thermometric sensitivity of about $5 \cdot 10^{-5}$.

The heat equivalent of the calorimeter is determined after each experiment and is, in effect, a measurement of the work done by the current in heating the calorimeter. For this purpose there is a heater of resistance about 13 ohms in the calorimeter. In order to determine the current strength, the differences of potential between the ends of the heater and of the standard 10-ohm resistance are measured with a compensator. The time is determined by the aid of a Gipp chronoscope.

The temperature of the jacket is controlled automatically, and for this purpose the Wheatstone bridge 5 and the photo-relay 6 are used. The bridge is composed of two constant resistances, each of 10 ohms, and two platinum resistance thermometers. One of the control resistance thermometers is placed in the calorimeter, and the other is placed in the jacket. Each control thermometer has a resistance of about 130 ohms at 70° . A mirror galvanometer, similar to the one already mentioned, is placed in the diagonal of the control bridge. The measuring and control Wheatstone bridges are supplied with a current of 0.1 amp from accumulators, and during an experiment this current is maintained constant within $5 \cdot 10^{-6} \text{ mA}$.

Measurements were carried out of the heats of reaction of isomeric chloroammines of bivalent platinum with aqueous ammonia (9.4%) at 70° . Of a group of seven isomeric chloroammines of bivalent platinum, five were investigated: two monomers - $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, the dimer $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2$ and two trimers - $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_3$ and $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)_3\text{Cl}_2]$. All the enumerated isomers have the empirical composition $\text{PtCl}_2 \cdot 2\text{NH}_3$. Owing to the specific behavior of the pink and green salts $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ in ammoniacal solution (the spontaneous change of the pink salt into the green and the very slow dissolution of the latter), only preliminary results were obtained for these salts, and these are not given here.

The salts employed were synthesized from spongy platinum and were carefully purified. Crystal-optical and chemical analyses showed that the salts prepared contained no impurities. The reactions proceeding in the calorimeter may be written in the following general form:

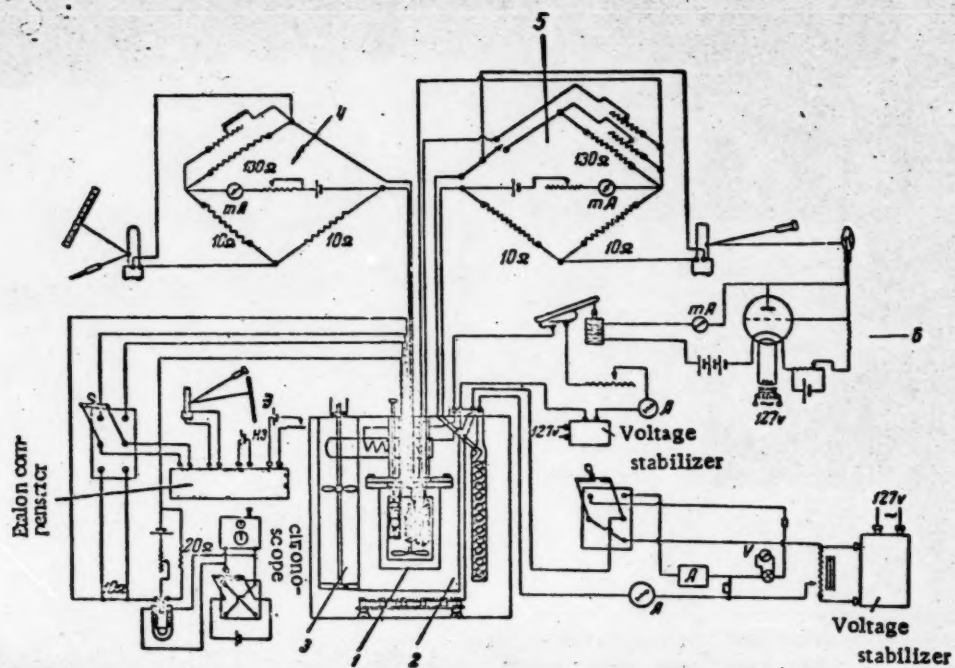


where $n = 1, 2$ or 3 . The quantities taken in all experiments were: ammonia solution, 210.0 g; salt, 0.3000 g.

The results of heat-of-reaction measurements for the five isomeric chloroammines of bivalent platinum are given in Tables 1-5. The values of Q in the second column of the tables are heats measured in the calorimeter. In the third column the departures of the measurements from the mean are given. In the fourth column the mean values of the measured heats are given.

It should be pointed out that the values of Q given in the tables contain a systematic error of about 7 cal/g. This error is associated with the presence of air in the ampoule containing the substance. When the ampoule was crushed, this "air bubble" became saturated with ammonia. The value of the thermal effect due to the "air bubble" was estimated in special experiments, and it was found to be sufficiently constant for ampoules of the volume employed. The difference of the measured heats for two isomers, without correction for the air bubble, gives the heat of isomerization (the difference in the total energies of the isomers), since the bubble effect is excluded at the same time.

The quantity Q_p , corrected for the "bubble effect", gives the heat of reaction of the salt with the ammonia solution. The error in this quantity is made up of the error in the measurement of Q and the error in the measurement of the "bubble effect." The values of the heats of reaction of isomeric platinum compounds with ammonia presents interest for its own sake, for from these, by the use of data in the literature, it is possible to calculate the heats of formation of the isomers. However, the data in the literature are given for a standard temperature (25°). As the specific heats of the compounds investigated are not known, it was possible to make only approximate calculations of the heats of reaction at 25° and to determine heats of formation of the isomers at this standard temperature.



General diagram of apparatus.

TABLE 1

Heat of reaction Q_1 of $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ with NH_3 solution:

Expt. No.	Q_1 (cal/g)	$Q_1 - \bar{Q}_1$	\bar{Q}_1
1	62.5 ₁	+ 0.13 ₈	62.3 ₇
2	61.9 ₄	- 0.43 ₂	
3	62.3 ₂	- 0.05 ₂	
4	62.7 ₂	+ 0.35 ₂	

Principal period of the experiments 4-5 minutes

TABLE 3

Heat of reaction Q_3 of $[\text{Pt(NH}_3)_3\text{Cl}][\text{Pt(NH}_3)_3\text{Cl}_2]$ with NH_3 solution

Expt. No.	Q_3 (cal/g)	$Q_3 - \bar{Q}_3$	\bar{Q}_3
1	61.6 ₆	- 0.1 ₁	61.7 ₇
2	62.2 ₂	+ 0.4 ₅	
3	62.5 ₂	- 0.2 ₅	
4	61.7 ₀	- 0.0 ₇	

Principal period of the experiments ~3.5 minutes

TABLE 5

Heat of reaction Q_5 of $[\text{Pt(NH}_3)_4][\text{Pt(NH}_3)_3\text{Cl}_2]$ with NH_3 solution

Expt. No.	Q_5 (cal/g)	$Q_5 - \bar{Q}_5$	\bar{Q}_5
1	58.3 ₃	- 1.1 ₄	59.4 ₇
2	60.6 ₇	+ 1.2 ₀	
3	59.8 ₂	+ 0.3 ₅	
4	59.0 ₈	+ 0.3 ₉	

Principal period of the experiments ~18 minutes

TABLE 2

Heat of reaction Q_2 of $\text{trans-[Pt(NH}_3)_2\text{Cl}_2]$ with NH_3 solution.

Expt. No.	Q_2 (cal/g)	$Q_2 - \bar{Q}_2$	\bar{Q}_2
1	52.1 ₈	+ 0.02 ₅	52.1 ₅₅
2	52.1 ₅	- 0.00 ₅	
3	52.1 ₉	+ 0.03 ₅	
4	52.1 ₈	- 0.05 ₅	

Principal period of the experiments ~4 minutes.

TABLE 4

Heat of reaction Q_4 of $[\text{Pt(NH}_3)_3\text{Cl}_2][\text{PtCl}_4]$ with NH_3 solution

Expt. No.	Q_4 (cal/g)	$Q_4 - \bar{Q}_4$	\bar{Q}_4
1	54.8 ₃	- 0.1 ₃	54.9 ₃
2	55.0 ₄	+ 0.1 ₁	
3	54.9 ₄	+ 0.0 ₁	

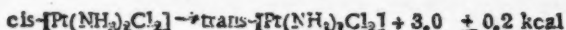
Principal period of the experiments ~20 minutes

DISCUSSION OF EXPERIMENTAL

RESULTS

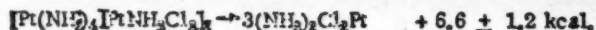
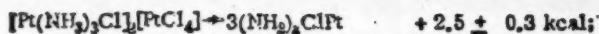
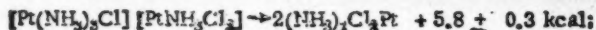
It will be seen from an examination of the results obtained that the trans monomer $[\text{Pt(NH}_3)_2\text{Cl}_2]$ has the least heat of reaction with ammonia. It may therefore be supposed that it is relatively the most stable isomer, i.e., all of the other isomers investigated should go over into the trans monomer with evolution of heat. By taking the differences of the heats of reaction with ammonia we obtain the heats of isomeriz-

ation. The heat of isomerization of the cis monomer into the trans monomer at 70° is 3.0 ± 0.2 kcal/mole.



This isomerization reaction has been effected directly by heating $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ to 170° [6].

The following isomerization (depolymerization) reactions may be predicted, the heats of reaction being obtained from our measurements (at 70°):



SUMMARY

1. A method has been proposed for the determination of the differences between the total energies of isomeric platinum chloroammines.

2. A hermetic calorimeter for liquids, having constant heat exchange and permitting measurements to be taken from room temperature to 100-120°, has been constructed. The thermometer of the calorimeter has a sensi-

tivity of the order of $5 \cdot 10^{-6}$. The calorimetric sensitivity of the apparatus is $1.5 \cdot 10^{-2}$ cal. The amount of complex compound required for the measurement is 0.1 - 0.3 g.

3. Measurements have been made of the heats of reaction of five chlorammines of bivalent platinum with aqueous ammonia (9.4% NH_3) at 70° , the probable error being about 1%. The heats of four isomeric changes have been estimated (probable error about 10%).

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COMPLEX COMPOUNDS OF PLATINUM WITH ACETAMIDE

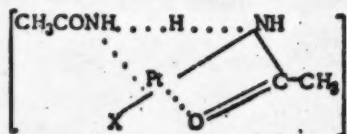
I. I. Chernyayev and L. A. Nazarova

One of the peculiarities of nonionic platinum-acetamide complexes of the form $[\text{PtNH}_2\text{COCH}_3 \cdot \text{NHCOCH}_3 \cdot \text{X}]$ where $\text{X} = \text{NO}_3, \text{Cl}, \text{Br}, \text{I}, \text{CNS}$, or NO_2 , is, as we have already pointed out [1], the notable difference in character between the linkage of the platinum with the two acetamide groups and that formed with the acidic addend. The latter, in spite of the evident complex nature of its bond with platinum, is very mobile and is comparatively readily replaced by various acidic atoms and groups, while at the same time all the original properties characteristic of platinum acetamide compounds remain unchanged. In contrast to the acid addend, the acetamide molecule and the acetamido group are firmly bound to the platinum, and furthermore, the acetamide groups appear to be inseparably attached to one another. When various chemical reagents react with the compound, either the grouping comprised of an acetamide molecule and an acetamido group remains unchanged, or the two groups are eliminated together, leading to formation of the usual platinum complex compounds. In spite of many attempts, it has not been found possible to replace any one of the acetamide groups by another addend. This peculiarity in the chemical behavior of the addends of platinum acetamide compounds opens up wide possibilities for the synthesis of compounds having various acidic addends. However, all the compounds are characterized by remarkable stability to such powerful oxidizing agents as aqua regia, gaseous chlorine, bromine, concentrated nitric acid, and so on. In contrast to all other known complex compounds of bivalent platinum, in this case oxidation of the platinum does not occur, and the reaction leads only to the replacement of one acidic addend by another, without any change in the acetamide grouping, i.e., conversion of one acetamide compound into another occurs.

This reaction, which has no parallel in the chemistry of the complex compounds of bivalent platinum, allows us to suppose that the anomalous properties of platinum acetamide compounds depend to a considerable extent on the acetamide grouping, firmly bound to platinum. The remarkable stability of this grouping is brought out particularly clearly in the reaction between platinum acetamide compounds and concentrated nitric acids. Only by long and intensive boiling with concentrated acid (sp. gr. 1.41) is it possible to bring these substances into solution, and from the solution, cooled and diluted with water, a nitratamidoamideplatinum separates. If the precipitate is immediately filtered off and an agent such as HCl, NH_4Br , NH_4CNS or NaNO_2 is added to the filtrate, then a precipitate of chloro-, cromo-, thiocyanato-, or nitro-amidoamideplatinum separates fairly rapidly. Such a course of reaction is in full accord with the low coordinating power of the group NO_3 , which shows a greater mobility in a nitratamidoamideplatinum than any of the other acidic addends, and is particularly readily replaced.

It was by this method that we synthesized a bromoamidoamideplatinum of homogeneous composition, which has not been done previously by the usual method (action of KBr on chloroamidoamideplatinum). The properties and chemical behavior of the bromoamidoamideplatinum not only confirm the far-reaching analogy of this compound with all other nonionic acetamide compounds, but also allow us to place it, on the basis of its reactivity, between the chloro- and iodo-amidoamideplatinums in the series of these compounds. Actually, if we arrange acetamide platinum compounds according to their reactivities, we obtain a kind of natural series, at the extremes of which are found compounds containing NO_2 and NO . All the remaining compounds follow one after the other in order of decreasing or increasing coordinating power, or of the magnitudes of the trans effects of the corresponding acidic addends: NO_2 , Cl , Br , I , CNS , and NO .

Thus, on the basis of the experimental results we may conclude that the greater the trans effect and coordinating power of an acidic addend, the less the reactivity of the corresponding nonionic acetamide platinum compound and the greater its stability. To what extent this relation is a manifestation of the trans-effect principle can only be determined on the basis of a thorough and careful study of the chemical nature of platinum acetamide compounds. Further study of the chemical nature of these compounds is essential also for the elucidation of the reasons for their anomalous properties, for the proposed structure of these compounds, which is expressed by the formula



In spite of the great tendency of ethylenediamine to occupy two coordination places with formation of a stable five-membered ring, in the present case it evidently occupies only one coordination position, and the acetamido-acetamide grouping is preserved unchanged. However, this question cannot be regarded as resolved, for some properties of the compounds obtained do not support this conclusion.

Thus, the presence of a free amino group in these compounds should be shown by an alkaline reaction in aqueous solution and increased electrical conductivity, but the solutions have a neutral reaction and the values of the conductivity are characteristic for typical two-ion electrolytes. We give here the results of conductivity determinations for these compounds; they were kindly carried out by V. M. Izuchevskaya.

Electrical conductivity of aqueous solutions of the amido(ethylenediamine)amido(II) nitrate at 25°:

ν (liter/mole)	μ
250	102.0
500	107.6
1000	111.8
2000	116.9
4000	120.0
8000	124.0

Electrical conductivity of the amido(ethylenediamine)amido(II) nitrite at 25°:

ν (liter/mole)	μ
500	117.0
1000	121.0
2000	124.3
4000	129.6

All the ethylenediamine-acetamide platinum compounds that we prepared had very similar properties and, at the same time, were considerably different in properties from the nonionic platinum acetamide compounds. Unlike the latter, the compounds prepared were so soluble that they could be isolated only from alcoholic solution. Aqueous solutions of the compounds had neutral reactions and the presence of the corresponding acid anions and complex cations could be confirmed. With potassium chloroplatinate (II) the ethylenediamine-acetamide platinum compounds formed yellow microscopic needlelike crystals, difficultly soluble in water.

We give here the analytical results for compounds obtained by the action of potassium chloroplatinate (II) on 1) the nitrate, 2) the chloride, 3) the bromide, 4) the iodide, 5) the thiocyanate, and 6) the nitrite.

Found %: 1) Pt 53.96; 54.44; Cl 12.83; 13.36.
 2) Pt 53.74; 54.41; Cl 12.45; 12.88.
 3) Pt 54.30; 54.36; Cl 12.53; 12.91.
 4) Pt 54.50; 54.05; 54.02; Cl 13.01.
 5) Pt 54.42; 54.07; Cl 12.80.
 6) Pt 54.88; 54.17; Cl 12.82.

$[\text{PtNH}_2\text{COCH}_2\text{NHCOCCH}_2\text{En}]_2[\text{PtCl}_4]$. Calculated %: Pt 54.11; Cl 13.15.

On the basis of the results obtained, the fact that the same compound is formed in all cases is established beyond dispute, and its composition confirms the identity of the inner spheres of all of the ethylenediamine-acetamide platinum compounds. The reaction leading to the formation of the chloroplatinate (II) can be expressed as follows:



where $\text{X} = \text{NO}_3$, Cl, Br, I, CNS or NO_2 .

In order finally to resolve the question whether a rearrangement occurs in the inner sphere of platinum acetamide compounds of the electrolyte type—opening of the acetamide ring and formation of an ethylenediamine ring—it is necessary to study the action of ammonia (typical of "amines" occupying one coordination position) on nonionic platinum acetamide compounds. The preparation of compounds analogous to the ethylenediamine-acetamide platinum compounds could be regarded as a proof of the absence of bond rearrangement and of the constancy of the acetamide grouping.

where $X = \text{NO}_3, \text{Cl}, \text{Br}, \text{I}, \text{CNS}, \text{or } \text{NO}_2$, cannot explain all their peculiarities in behavior. However, the direct study of nonionic compounds is rendered difficult by their exceptionally poor solubility, and it has consequently been necessary to have recourse to electrolyte types. The synthesis of such compounds is of particular interest also for the solution of the question whether the anomalous properties of the compounds discussed above are peculiar to the nonelectrolyte type, or are preserved also in ionic compounds of good solubility.

EXPERIMENTAL

Reaction of Platinum Acetamide Compounds with Ethylenediamine

A classical method for the preparation of ionic bivalent platinum compounds consists in treating nonelectrolytes with amines [2]. The reaction may lead to the formation of compounds containing from one to four molecules of amine, according to the number of amine molecules introduced into the inner sphere of the complex compound. As far as platinum acetamide compounds are concerned, certain peculiar properties, in particular the presence of a readily replaceable acidic addend in the inner sphere, encourage replacement by the amine of this addend. Particular interest is presented by the question whether the stability, characteristic of platinum acetamide compounds, of the acetamido-acetamide grouping and their mutual linkage will be preserved in this reaction, or will it be possible, by the use of an amine such as ethylenediamine, to replace one of the acetamides? In view of these problems, ethylenediamine and ammonia were employed in the investigation. Previous experiments had shown that, in the cold, ethylenediamine does not react appreciably with platinum acetamide compounds of the nonionic type, while strong heating leads to elimination of both acetamide molecules with formation of platinum ethylenediamine compounds. It was necessary to try to find intermediate conditions under which there was a chance of the formation of mixed ethylenediamine-acetamide platinum compounds. As a result of a large number of experiments, such conditions were found, and ethylenediamine-acetamide compounds of platinum were isolated in the form of pale-yellow, finely crystalline precipitates. It should be noted that, in spite of the great similarity in properties and behavior of the initial platinum acetamide compounds, their individual character is manifest also in their reactions with ethylenediamine.

In full accord with its high reactivity, the nitratoamidoamideplatinum readily dissolved when warmed slightly with an aqueous solution of ethylenediamine, taken in slight excess over equimolecular quantities. When insufficient ethylenediamine was taken, then on evaporation of the solution separation of some of the original nitratoamidoamideplatinum was observed. All the remaining platinum acetamide compounds dissolved only after long heating with ethylenediamine solutions. It is recommended that a great excess of ethylenediamine should be avoided, as it leads to formation of ethylenediamine compounds of formula $[\text{PtEn}_2]\text{X}_2$, where $X = \text{Cl}, \text{Br}, \text{I}, \text{or } \text{CNS}$.

We give here the analytical results on compounds prepared by the action of ethylenediamine on 1) the chloroamidoamideplatinum, 2) the nitratoamidoamideplatinum, 3) the bromoamidoamideplatinum, 4) the iodoamidoamideplatinum, 5) the thiocyanatoamidoamideplatinum, and 6) the nitroamidoamideplatinum:

$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]\text{Cl}$	1. Found %: Pt 47.54; 48.38; Cl 8.86; 8.40 Calculated %: Pt 47.89; Cl 8.74
$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]\text{NO}_3$	2. Found %: Pt 45.24; 44.50; N 15.40 Calculated %: Pt 44.93; N 16.12
$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]\text{Br}$	3. Found %: Pt 43.81; 42.99; Br 18.65 Calculated %: Pt 43.14; Br 17.73
$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]\text{I}$	4. Found %: Pt 38.36; 39.27; 39.29 Calculated %: Pt 39.07
$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]\text{CNS}$	5. Found %: Pt 45.12; 45.87 Calculated %: Pt 45.34
$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]\text{NO}_2$	6. Found %: Pt 47.11; N 16.20; 16.60 Calculated %: Pt 46.65; N 16.74

On the basis of the analytical results on the compounds obtained it may be supposed that in the reaction of ethylenediamine with nonionic platinum acetamide compounds the ethylenediamine is taken into the inner sphere and the acidic addends are displaced into the outer sphere, as indicated by the following equation:



where $X = \text{NO}_3, \text{Cl}, \text{Br}, \text{I}, \text{CNS}$ or NO_2 .

In spite of the great tendency of ethylenediamine to occupy two coordination places with formation of a stable five-membered ring, in the present case it evidently occupies only one coordination position, and the acetamido-acetamide grouping is preserved unchanged. However, this question cannot be regarded as resolved, for some properties of the compounds obtained do not support this conclusion.

Thus, the presence of a free amino group in these compounds should be shown by an alkaline reaction in aqueous solution and increased electrical conductivity, but the solutions have a neutral reaction and the values of the conductivity are characteristic for typical two-ion electrolytes. We give here the results of conductivity determinations for these compounds; they were kindly carried out by V. M. Izuchevskaya.

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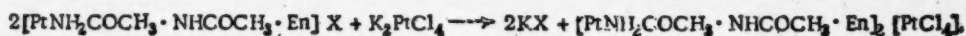
All the ethylenediamine-acetamide platinum compounds that we prepared had very similar properties and, at the same time, were considerably different in properties from the nonionic platinum acetamide compounds. Unlike the latter, the compounds prepared were so soluble that they could be isolated only from alcoholic solution. Aqueous solutions of the compounds had neutral reactions and the presence of the corresponding acid anions and complex cations could be confirmed. With potassium chloroplatinate (II) the ethylenediamine-acetamide platinum compounds formed yellow microscopic needlelike crystals, difficultly soluble in water.

We give here the analytical results for compounds obtained by the action of potassium chloroplatinate (II) on 1) the nitrate, 2) the chloride, 3) the bromide, 4) the iodide, 5) the thiocyanate, and 6) the nitrite.

Found %: 1) Pt 53.96; 54.44; Cl 12.83; 13.36.
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$[\text{PtNH}_2\text{COCH}_3\text{NHCOCH}_3\text{En}]_2[\text{PtCl}_4]$. Calculated %: Pt 54.11; Cl 13.15.

On the basis of the results obtained, the fact that the same compound is formed in all cases is established beyond dispute, and its composition confirms the identity of the inner spheres of all of the ethylenediamine-acetamide platinum compounds. The reaction leading to the formation of the chloroplatinate (II) can be expressed as follows:



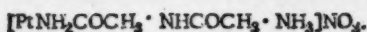
where X = NO₃, Cl, Br, I, CNS or NO₂.

In order finally to resolve the question whether a rearrangement occurs in the inner sphere of platinum acetamide compounds of the electrolyte type—opening of the acetamide ring and formation of an ethylenediamine ring—it is necessary to study the action of ammonia (typical of "amines" occupying one coordination position) on nonionic platinum acetamide compounds. The preparation of compounds analogous to the ethylenediamine-acetamide platinum compounds could be regarded as a proof of the absence of bond rearrangement and of the constancy of the acetamide grouping.

Reaction of Platinum Acetamide Compounds with Ammonia

It was known from previous investigations that a chloroamidoamideplatinum does not react with ammonia even after prolonged heating, and investigation was therefore directed to the most reactive compound, the nitrat-amidoamideplatinum. Experiment showed that on merely being warmed with concentrated ammonia the compound dissolves, forming a yellowish solution. On evaporation of the solution to dryness and treatment of the dry residue with alcohol, it was found possible to crystallize the compound in the form of pale-yellow plates. In order to obtain homogeneous compounds, it was found necessary to carry out the evaporation of the ammoniacal solutions of the platinum acetamide compounds in presence of an excess of ammonia; otherwise, the reverse reaction occurs, and the original nitratamidoamideplatinum separates.

Analysis gave:



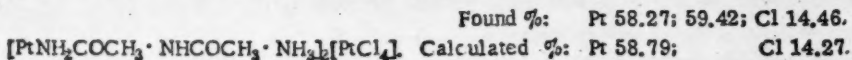
Found %: Pt 50.58; 50.16.

Calculated %: Pt 49.92.

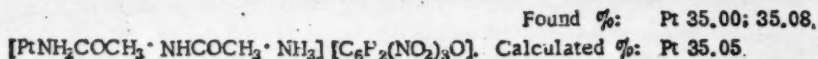
The electrical conductivity, determined in M. M. Yakshin's laboratory by his assistant V. M. Ezuchevskaya, characterizes the compound as a two-ion electrolyte, which is in agreement with the proposed structure.

\bar{v} (liter/mole)	μ
500	91.3
1000	100.5
2000	103.6
4000	106.2
8000	110.4
16000	111.7

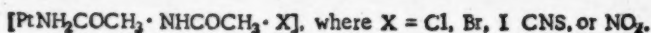
The properties of the compound are very close to those of the amido(ethylenediamine)amido-platinum (II) nitrate. Aqueous solutions of the compound form yellow microscopic needlelike crystals of low water-solubility with potassium chloroplatinate (II) and with sodium picrate. The analytical results for the chloroplatinate (II) are:



The analytical results for the derivative formed by the amidoammineamideplatinum (II) nitrate with sodium picrate are:



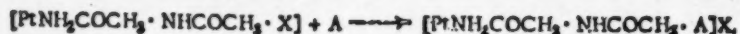
Thus, it may be considered, on the basis of the experimental results, that when ammonia reacts with the nitratoamidoamideplatinum the acidic addend is eliminated into the outer sphere and ammonia is taken up in the inner sphere with formation of a compound analogous to the amido(ethylenediamine)amideplatinum (II) nitrate. However, it was of interest to find out whether the character of the reaction is preserved also when ammonia reacts with various nonionic platinum acetamide compounds. With this aim, a study was made of the reaction of ammonia with compounds of formula



As a result of numerous experiments it was established that all these compounds dissolved, with varying degrees of difficulty, in concentrated ammonia with formation of pale-yellow solutions. The chloro-, thiocyanato, and nitro-amidoamidoamidoplatinums were particularly difficult to dissolve. In order to dissolve the chloroamidoamidoamido platinum, it was necessary to treat the residues repeatedly with concentrated ammonia.

It was not found possible to isolate the ammonia-acetamide platinum compounds in the pure state, for during the evaporation of the ammoniacal solutions the reverse reactions, giving the original compounds, occur very readily. However, the compounds were characterized in the form of the derivatives formed with sodium picrate, which form microscopic yellow needles of low solubility in water.

Summarizing all the experimental results obtained in the study of the action of ethylenediamine and of ammonia on nonionic platinum acetamide compounds, we may conclude that the character of the reaction is evidently the same in all cases and consists of the elimination of acidic addends and the reception into the inner sphere of the respective amine. The mechanism of the reaction may be expressed by the following general equation:



where A = NH₂ or NH₂·CH₂·CH₂·NH₂; X = NO₃, Cl, Br, I, CNS, or NO₂.

In spite of the fact that ethylenediamine occupies only one coordination position, the ethylenediamine-acetamide platinum compounds are more stable than the ammonia-acetamide compounds, which is quite non-characteristic for complex compounds of bivalent platinum. It is well known that in these compounds the link between ammonia and platinum is notable for its high strength.

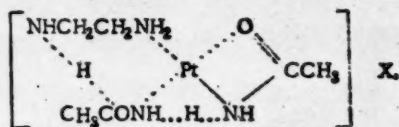
We present here the analytical results for compounds obtained by the action of sodium picrate on 1) the amidoammineamideplatinum (II) chloride, 2) the amidoammineamideplatinum (II) bromide, 3) the amidoammineamideplatinum (II) thiocyanate, 4) the amidoammineamideplatinum (II) iodide, and 5) the amidoammineamideplatinum (II) nitrite.

Found %: 1) Pt 35.15
2) Pt 35.10
3) Pt 34.75; N 14.59
4) Pt 34.81
5) Pt 35.13;

[PtNH₂COCH₃·NHCOCH₃·NH₂][C₆H₃(NO₂)₃O]. Calculated %: Pt 35.05; N 15.07.

The analytical results for these compounds show that the same derivative is formed in all cases, its composition being at the same time identical with that of the picrate derivative of the amidoammineamido-platinum (II) nitrate. Thus, there is every reason to suppose that ethylenediamine occupies only one coordination position in the platinum acetamide compounds.

The high stability of ethylenediamine-acetamide compounds of platinum and the peculiar behavior of ethylenediamine in the inner sphere of the compounds may be partially explained if the possibility is admitted of the formation of a hydrogen bond between the nitrogen of the free NH₂ group and the oxygen of the neighboring acetamide, as indicated in the following scheme:



where X = NO₃, Cl, Br, I, CNS or NO₂.

SUMMARY

1. A study has been made of the action of amines (ethylenediamine and ammonia) on nonionic platinum acetamide compounds, and it has been shown that these nonelectrolytes may be converted into compounds of the electrolyte type.

2. Ethylenediamine-acetamide and ammonia-acetamide platinum compounds have been synthesized; their structures may be represented by the following formulas: [PtNH₂COCH₃·NHCOCH₃·A]X, where A = En and NH₂; X = NO₃, Cl, Br, I, CNS or NO₂.

3. It has been suggested that in the ethylenediamine-acetamide platinum compounds there is a hydrogen bond between the nitrogen of the free amino group and the oxygen of the neighboring acetamide.

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Inorganic Chemistry of the USSR Academy
of Sciences

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- [2] A. A. Grinberg, "Introduction to the Chemistry of Complex Compounds", State Chem. Press, 1951.

REACTIONS IN SOLUTIONS OF BIVALENT PLATINUM DIAMMINES IN PRESENCE OF ULTRAVIOLET RADIATION

A. V. Babaeva and M. A. Mosyagina

A number of investigations, including ours, have shown that the absorption spectra of the majority of typical complex compounds, such as those of the platinum metals, cobalt and chromium, in the visible and ultraviolet regions consist of two or three bands. Sometimes there are no absorption bands in the visible region, so that the substance is colorless, or there may be continuous structureless absorption in the ultraviolet.

It may be regarded as established that the frequencies of the maxima of the second band, which lies in the ultraviolet region, have the effect of producing in the substance a peculiar, incomplete dissociation of the substituent and may serve as a measure of the strength of the coordinate link. For example, these frequencies bring about the decomposition of potassium trioxalatocobaltate (III), and accelerate the hydrolysis of oxalatopentamminecobalt (III) sulfate and the formation of chloropentammineplatinum (IV) chloride. The number of known photochemical reactions of this kind for complex compounds is, however, as yet small.

The classical compound — cis-dichlorodiammineplatinum, or so-called Peyrone's salt — is a compound that is fairly stable under various conditions: it is decomposed at 340°, being first converted at 290° into the trans isomer [1]; it does not undergo visible change in the light either in solution or in the crystals; in aqueous solution it is hydrated and hydrolyzed, as the rise of electrical conductivity with time shows [2], but from the acidified solution the compound may be readily recrystallized, heating being applied almost up to the boil.

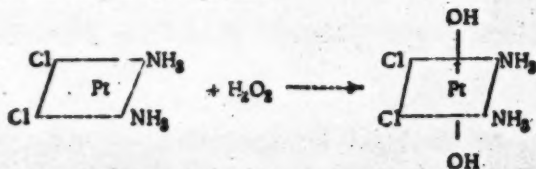
The absorption spectrum of the cis-dichlorodiammine in the visible and ultraviolet regions was studied by Liefshitz and Rosenbohm [3] in 1921. They found that the compound has only one absorption band having a maximum at 3700 Å. According to our results [4], the spectrum of cis-dichlorodiammineplatinum in this region consists of three bands having maxima at 3660, 3080 and 2730 Å. If the absorption of photons of ultraviolet frequency is indeed associated with distension of the bond between the central atom and the substituent, then it may be supposed that by irradiation of cis-dichlorodiammineplatinum with these frequencies in presence of water, there should be increased hydrolysis.

We set ourselves the task of investigating whether photochemical reactions do occur in a solution of this salt under the action of ultraviolet radiation, to what these reactions lead, and what frequencies are responsible for them.

EXPERIMENTAL

A saturated aqueous solution of the cis-dichlorodiammine $[(\text{NH}_3\text{Cl})_2\text{Pt}]$ (solubility at 25°, 0.25%) was irradiated in a quartz vessel by the unfiltered radiation from a quartz mercury lamp. After 20-30 minutes, black amorphous material resembling metallic platinum began to precipitate from solution. It was quite insoluble in water and in sulfuric acid, but it dissolved in dilute hydrochloric acid not only on heating, but also in the cold. As irradiation of the original solution proceeded, its acidity increased. Also, the temperature in the reaction vessel rose, of course. Performance of the experiment in a special quartz vessel having water cooling and stirring showed that lowering of temperature encourages formation of the black precipitate.

It is known that when short-wave ultraviolet acts on water hydrogen peroxide is formed, which in our experiment, without cooling, was evidenced by the copious evolution of oxygen. A relevant hypothesis would be the oxidation of the platinum diammine according to the equation:



if the properties of the compound formed did not differ greatly from those of dichlorodihydroxodiammineplatinum, which is of a pale yellow color. The hydrolysis products from diammines are distinct also in other properties. Thus, neither hydrolysis nor oxidation with hydrogen peroxide will convert the dichlorodiammineplatinum into a black substance, and it is possible that its appearance must be ascribed to both processes acting simultaneously with participation of the energy of the ultraviolet rays.

What frequencies are responsible for this reaction and what is the substance formed? By the application of a light filter consisting of a solution of cobalt chloride in acetone, which absorbs radiation of wavelength less than 3000 Å, no change could be induced in the solution, even after many hours of irradiation. Again, no black substance was formed when irradiation was effected through a solution of nickel chloride, which passes only the band of waves between 2300 and 2500 Å. In short, the frequencies that are active for the compound investigated correspond to wavelengths lying between 2500 and 3000 Å, i.e., those which are absorbed to give a band in the absorption spectrum having a maximum at 2730 Å, and also wavelengths of less than 1900 Å, which cause the photochemical formation of hydrogen peroxide from water.

In order to establish the composition of the compound formed, the black precipitate was filtered off, carefully washed with boiling water to remove traces of the original salt, and analyzed. Platinum was determined in this substance by reducing a weighed amount by evaporating down with sulfuric acid and igniting; chlorine was estimated as silver chloride in a weighed sample that was reduced by heating with sodium carbonate; and nitrogen was determined by the combustion of a micro quantity. When determining water by drying, we found that it vaporized away continuously as the temperature rose from 50 to 200° and higher. It may therefore be supposed that it was being removed also from the inner sphere.

Analytical Results

Found %: Pt 70.30, 70.74, 70.10; mean 70.38

Found %: Cl 9.25, 9.13, 9.41; mean 9.26

Found %: N 5.14, 5.21; mean 5.18

We did not succeed in determining whether the substance was an electrolyte or not, for it was impossible to determine its electrical conductivity owing to its insolubility in water.

When the black precipitate was dissolved in dilute hydrochloric acid, a cherry-red solution was obtained, from which, when heated on a water bath for thirty minutes, crystals of ammonium chloroplatinate (IV) separated. Ammonium trichlorodiammineplatinate (II) was extracted from the solution that had been concentrated on the water bath. The compositions of these compounds were confirmed by analysis for platinum.

Found %: Pt 44.01, 44.25

$(\text{NH}_4)_2\text{PtCl}_6$ Calculated %: Pt 43.94

Found %: Pt 55.56

$\text{NH}_4[\text{NH}_3\text{Cl}_3\text{Pt}]$ Calculated %: Pt 55.05

From the hydrochloric acid solution the monoammine was isolated also by means of a solution of $[(\text{NH}_4)_4\text{Pt}]_2\text{Cl}_2$ in the form of the tetrammine salt $[(\text{NH}_4)_4\text{Pt}][\text{NH}_3\text{Cl}_3\text{Pt}]_2$, which formed light brown scalelike crystals.

Found %: Pt 64.75, 64.60, 65.12.

$[(\text{NH}_4)_4\text{Pt}][\text{NH}_3\text{Cl}_3\text{Pt}]_2$ Calc. %: Pt 64.71

The investigated compound, when oxidized with chlorine in aqueous suspension, became brown. From a solution of the brown substance in dilute hydrochloric acid ammonium chloride caused the precipitation of chloroplatinate (IV), and from the mother liquor yellow prisms of $\text{NH}_4[\text{NH}_3\text{Cl}_3\text{Pt}]\text{H}_2\text{O}$ crystallized out, the platinum content being 48.56%, and the water content 3.66% (calculated from the formula: platinum 47.96%, water 4.23%).

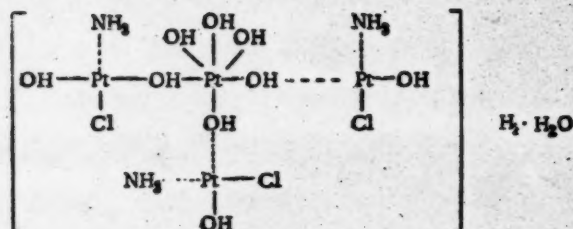
It follows from these experiments that both bi- and quadri-valent platinum enter into the composition of the compound formed by the action of ultraviolet radiation on Peyrone's salt. In order to establish the bi-quadri ratio, the substance was oxidized quantitatively with potassium permanganate. For this purpose, diluted (1:2) hydrochloric acid was added dropwise to a weighed amount of the compound, the reaction mixture being heated on a water bath. Then, as usual, sulfuric acid was added and the solution was titrated potentiometrically with permanganate.

Found %: Pt 51.87, 53.63; mean 52.70

As the platinum content of the investigated substance was 70.38%, it follows that the ratio of Pt^{IV} to Pt^{II} was about 1:3, and the ratio Pt:Cl:N was about 4:3:3.

From a comparative examination of the analytical results and the properties of the product of the irradiation of cis-dichlorodiammineplatinum the conclusion may be drawn that the product is evidently a polynuclear compound of bi- and quadri-valent platinum containing water of crystallization, during the estimation of which by drying, a portion of water is removed also from the inner sphere, where it is fixed in the form of hydroxyl groups attached to the platinum atom. There is nothing surprising in this behavior of hydroxyl groups, for it is characteristic of the radical of the hexahydroxo acid $[Pt(OH)_6]$, which is present in this compound. Evidently, the bivalent platinum atoms are linked with the quadrivalent platinum by hydroxyl bridges, which are ruptured by reaction with hydrochloric acid.

This compound must probably be assigned the following structure:



A compound of this structure should contain 70.27% platinum, 9.26% chlorine, 3.78% nitrogen; analysis gave 70.38% platinum, 9.37% chlorine, 5.21% nitrogen.

Irradiation by ultraviolet rays of the monoammine $K[NH_3Cl_3Pt]$ also led to a compound of similar composition.

Found %: Pt 70.30, 70.17, Cl 8.31

In a solution of trans-dichlorodiammineplatinum, which is characterized, according to our results [4], by an absorption spectrum having absorption maxima at 3760, 3170 and 2730 Å, the action of ultraviolet radiation also leads to reaction, leading to formation of a precipitate of brown color. However, the rate of this reaction is so low that a two-month irradiation was necessary in order that sufficient substance could be accumulated for investigation purposes.

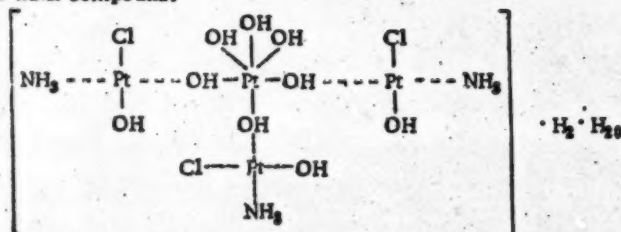
This, like the previous substance, dissolves in dilute hydrochloric acid, from which, on addition of ammonium chloride, ammonium chloroplatinate (IV) is precipitated; addition of a solution of tetrammineplatinum (II) chloride $[(NH_3)_4Pt]Cl_2$ leads to precipitation of a mixture of Magnus's salt $[(NH_3)_4Pt][PtCl_4]$, $[(NH_3)_4Pt][NH_3Cl_3Pt]$ and $[(NH_3)_4Cl_2Pt]Cl_2$, which are formed as a result of the following reactions:

1. $H_2PtCl_6 + [(NH_3)_4Pt]Cl_2 \rightarrow [(NH_3)_4Pt][PtCl_4] + [(NH_3)_3Cl_2Pt]Cl_2 + HCl$
2. $[NH_3Cl_3Pt]^- + [(NH_3)_4Pt]^{++} \rightarrow [(NH_3)_3Pt][NH_3Cl_3Pt]$

Analytical results for the brown compound:

Found %: Pt 70.24, 70.20, 70.16
Found %: Cl 8.70, 8.89
Found %: N 4.16, 4.15

Titration with potassium permanganate gave about 1:3; for the ratio $Pt^{IV} : Pt^{II}$. We consider it possible to assign the following structure, analogous to that for the compound obtained from cis-dichlorodiammineplatinum to the substance derived from the trans compound:



SUMMARY

1. It has been shown that in solutions of cis- and trans-dichlorodiammineplatinum the presence of ultraviolet radiation leads to the formation of polynuclear compounds of bi- and quadri-valent platinum having hydroxyl bridges.

2. The active frequencies correspond to the absorption band of these compounds having a maximum at 2730 Å.

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COMPLEX COMPOUNDS OF PLATINUM WITH DIALLYLAMINE

A. M. Rubinshtein and G. V. Derbisher

The first reference to complex compounds of platinum with unsaturated molecules occurred in 1829. By treating platinous chloride with alcohol and then with potassium chloride or ammonium chloride, Zeise obtained crystalline salts, the chemical composition of which he expressed by the formula $\text{Me}[\text{PtC}_2\text{H}_4\text{Cl}_2] \cdot \text{H}_2\text{O}$. At that time a number of chemists doubted the existence of these compounds, which were soon forgotten, but the existence of these substances, which had been described by Zeise in 1829, received some confirmation in 1861, when it was found that the gas evolved when such compounds are heated is ethylene C_2H_4 .

In 1861 Birnbaum obtained the salt $\text{Me}[\text{PtC}_2\text{H}_4\text{Cl}_2] \cdot \text{H}_2\text{O}$ by direct synthesis from ethylene and platinous chloride, and later a number of investigators more or less successfully examined the question of preparing analogous compounds. The investigations of Jorgensen must probably be considered as the most important of these studies; they again confirmed the correctness of Zeise's formulas and established that analogous properties are possessed by the salts $\text{Me}[\text{PtC}_2\text{H}_4\text{Cl}_2]$ and the salts $\text{Me}[\text{PtAX}_2]$, where A is an amine and X is Cl or Br , etc.

These analogies, when the peculiar features of ethylene compounds were neglected, placed the compounds in the general series of amines. Numerous researches by a number of other investigators on the compounds of platinum with ethylene homologs and unsaturated aromatic compounds gave reason for the postulation of the existence of a special class comprising compounds of this type. However, the absence in these investigations of systematic treatment and definite aim, and sometimes also inadequate care in carrying out the experiments, did not permit the place of these compounds in the general array of complex compounds to be established.

The first complete and systematic investigation of the complex compounds of platinum with unsaturated molecules was carried out in the Kurnakov Institute of General and Inorganic Chemistry by Chernyaev and Gelman [1]. Later, in an extensive investigation, Gelman [2] synthesized and investigated compounds of platinum with ethylene and some of its homologs, with compounds of the butadiene type, with diallyl, with nitric oxide, with carbon monoxide, etc. It was then found that substituents having double bonds had increased trans activity. It was established also that, in compounds having two double bonds, each individual bond can participate in complex formation, but the molecule of the unsaturated compound does not form a ring with the central atom. It was shown in this work that all the investigated unsaturated molecules form complex compounds only with bivalent platinum, that it is impossible to prepare compounds containing two or more unsaturated molecules in the inner sphere, and that the unsaturated molecules cannot form closed rings with the platinum.

The experiments carried out earlier by Rubinshtein [3,4] on the complex compounds of platinum with amines such as α - and β -aminopyridines and aminohalopyridines again did not result in the preparation of compounds having an inner-sphere ring. Each amine occupied one coordination position.

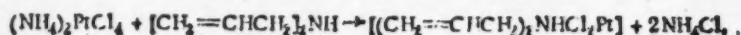
The present investigation is devoted to complex compounds of platinum with diallylamine. The study of complex compounds of this type is of significance in connection with the question of ring formation in complex compounds. Diallylamine is of special interest as a substituent in the present case, for it is unsaturated. Hitherto, in the complex compounds of platinum, no cases of the ring closure of unsaturated compounds have been observed. In the case of diallylamine it might be expected that complex compounds of cyclic structure could be formed, since here both the nitrogen of the NH group and the double bonds can participate in complex formation.

Our investigations show that under defined conditions diallylamine forms stable complex compounds of cyclic structure with platinum. The properties of these compounds have been studied, and inner-sphere substitution reactions and the conditions required for the making and breaking of the diallylamine ring have been studied. It has been found in the course of the work that diallylamine gives cyclic complex compounds only by reaction with ammonium chloroplatinate (II) and only in neutral medium. In acid medium, and also when potassium chloroplatinate (II) is used, the reaction with diallylamine has a completely different course.

EXPERIMENTAL

I. Study of the Reaction of Diallylamine with Ammonium Chloroplatinate (II)

The calculated amount of diallylamine, as required by the reaction



(one molecule of diallylamine to one molecule of chloroplatinate (II) was added in the cold to a saturated neutral solution of ammonium chloroplatinate (II) (in formulas, diallylamine $(\text{CH}_2=\text{CHCH}_2)_2\text{NH}$ will in future be denoted by D). Dichloro(diallylamine)platinum DCl_2Pt began to separate as a dark yellow precipitate as soon as the solutions were mixed. The salt was filtered off and dried in a desiccator at ordinary temperature, for all diallylamine compounds decompose at elevated temperatures. When the dark yellow salt had been filtered off, a second, light yellow salt separated. It was established by crystal-optical analysis that both salts were free from impurities and had refractive indices of 1.68 (dark yellow) and 1.72 (light yellow).

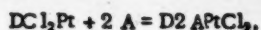
Chemical analysis showed that both salts had the same contents of platinum, chlorine and nitrogen. Whereas the dark yellow salt gave Pt 53.57, 53.67%; Cl 19.90, 19.87%; N 5.04%; the light yellow salt that separated in the second stage of the reaction between diallylamine and ammonium chloroplatinate (II) gave Pt 53.51, 53.30%; Cl 19.29%; N 4.18, 4.57%.

The calculated values for a compound of formula DCl_2Pt are Pt 53.78%; Cl 19.52%; N 3.85%. In spite of their identity in percentage composition, the two salts are distinct in color and solubility (the dark yellow salt is not readily wetted by water and is insoluble; the solubility of the light yellow salt is 0.040 g per 100 g of solution), and also in refractive index (dark yellow 1.68; light yellow 1.72). By analogy with the reaction of ammonium chloroplatinate (II) with ammonia, as a result of which cis-dichlorodiammineplatinum $(\text{NH}_3)_2\text{Pt}$ and its dimer $[\text{4NH}_3\text{Pt}][\text{PtCl}_4]$ are formed, we supposed that in this case also a monomer, the dark yellow salt DCl_2Pt , and a dimer, the light yellow salt $[\text{D}_2\text{Pt}][\text{PtCl}_4]$ are formed. This supposition was confirmed by the formation of the salt $[\text{D}_2\text{Pt}][\text{PtCl}_4]$ on addition of chloroplatinate (II) to a solution obtained by the action of an excess of diallylamine on DCl_2Pt . In order to prove the identity of the two salts we determined their solubilities: the respective values were 0.040 and 0.035 g per 100 g of solution.

Thus, by the action of diallylamine on ammonium chloroplatinate (II) in neutral solution, two compounds DCl_2Pt and $[\text{D}_2\text{Pt}][\text{PtCl}_4]$ were obtained; in these diallylamine occupies two coordination positions and consequently forms a ring.

Reactions of dichloro(diallylamine)platinum with ammonia and with pyridine.

A study of the reactions of dichloro(diallylamine)platinum DCl_2Pt with ammonia and with pyridine yielded confirmatory evidence of the existence and stability of the diallylamine ring. When DCl_2Pt was warmed carefully with ammonia or pyridine, the salt dissolved with formation of a reddish-brown (for ammonia) or brownish-yellow (for pyridine) solution. Evaporation of the solution yielded a dark brown or orange-red salt (respectively). If we suppose that the reaction of diallylamine with an amine proceeds according to the equation



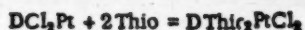
where $\text{A} = \text{NH}_3$ or Py , then we have for the salts obtained:

	Found %:	Pt 49.01, 48.19;	Cl 18.17, 18.40;	N 10.49, 10.20
$\text{D}(\text{NH}_3)_2\text{PtCl}_2$	Calculated %:	Pt 49.14	Cl 17.84	N 10.57
	Found %:	Pt 37.35,	Cl 14.10,	N 8.74, 8.62
$\text{DPy}_2\text{PtCl}_2$	Calculated %:	Pt 37.43	Cl 13.59	N 8.05

The two mixed amine-diallylamine compounds were obtained also by neutralization of solutions of $\text{D}(\text{NH}_3)_2\text{PtCl}_2$ and $\text{DPy}_2\text{PtCl}_2$ with hydrochloric acid. Also, they were isolated and characterized in the form of a chloroplatinate (II) $[\text{D}_2\text{Pt}][\text{PtCl}_4]$.

Reaction of dichloro(diallylamine)platinum with thiourea.

When a saturated solution of thiourea (it is indifferent whether the calculated amount or an excess of thiourea is used) reacted with dichloro(diallylamine)platinum DCl_2Pt , the salt dissolved and a dark red-brown solution was formed. When this solution was evaporated, a dark-colored precipitate separated and was washed carefully with alcohol to free it from excess of thiourea. Chemical analysis of the dry salt gave Pt 37.60%, 37.73%; N 13.83%. If we suppose that the reaction between thiourea and DCl_2Pt proceeds according to the equation:



calculation for $\text{DThio}_2\text{PtCl}_2$ gives Pt 37.88%, N 13.59%. Thus, even under the action of thiourea the diallylamine ring is not destroyed.

Action of hydrochloric acid on DCl_2Pt and the opening of the diallylamine ring.

In the compounds that we have just discussed, diallylamine occupies two coordination positions. It was of considerable interest to find conditions for the preparation of compounds in which diallylamine would occupy only one coordination position. With this purpose a study was made of the reaction of hydrochloric acid on dichloro(diallylamine)platinum DCl_2Pt and on the mixed ammonia-diallylamine tetrammine $\text{D}(\text{NH}_3)_2\text{PtCl}_2$. It was found that hydrochloric acid (1:2) applied at the boil caused the opening of the diallylamine ring of DCl_2Pt , yielding a compound of composition HDCl_3Pt , in which the diallylamine is contained in a complex anion. Chemical analysis of the compound obtained gave the following results:

	Found %: Pt 48.98, 49.52, 48.78, 49.47; Cl 27.23, 26.75; N 3.51, 3.76
HDCl_3Pt	Calculated %: Pt 48.83; Cl 26.66, N 3.50

By the action of the tetrammine chloride $[(\text{NH}_3)_4\text{Pt}]\text{Cl}_2$ on a hydrochloric acid solution of DCl_2Pt , the salt $[(\text{NH}_3)_4\text{Pt}][\text{DCl}_2\text{Pt}]$ was precipitated; its composition was established by analysis:

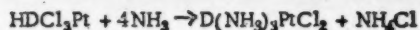
	Found %: Pt 55.73, 55.15; N 7.44
$[(\text{NH}_3)_4\text{Pt}][\text{DCl}_2\text{Pt}]$	Calculated %: Pt 55.21, N 7.92

The presence in this salt of the cation $[(\text{NH}_3)_4\text{Pt}]^{++}$ was readily revealed by treatment at the boil with chloroplatinate (II). The characteristic green salt $[(\text{NH}_3)_4\text{Pt}][\text{PtCl}_4]$ was then formed. Thus, boiling with hydrochloric acid (1:2) leads to opening of the diallylamine ring.

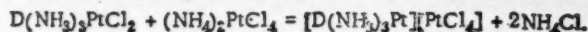
The reactions of the compound HDCl_3Pt (monoammine I) with ammonia, thiourea and caustic alkali were studied.

a) Reaction with ammonia.

When the compound HDCl_3Pt was carefully warmed with ammonia, it dissolved, and when the solution obtained was evaporated a dark brown precipitate separated. The precipitate was not homogeneous, and its composition could therefore not be determined. Treatment with water caused part of the precipitate to dissolve, giving a solution that gave a precipitate with ammonium chloroplatinate (II). We considered that the reaction between ammonia and monoammine I, HDCl_3Pt , proceeds as follows:



and further:



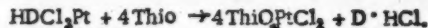
Analysis confirmed our supposition:

	Found %: Pt 57.12, 57.24; N 7.89
$[\text{D}(\text{NH}_3)_3\text{Pt}][\text{PtCl}_4]$	Calculated %: Pt 57.67, N 8.23

By the action of ammonia on monoammine I, HDCl_3Pt , a mixed tetrammine is obtained in which diallylamine again occupies one coordination position.

b) Reaction with thiourea.

A saturated solution of thiourea partly dissolved the mono ammine HDCl_3Pt even in the cold, but for complete dissolution it was necessary to heat to the boil. When dissolution was complete, the solution was allowed to evaporate freely. The precipitate that separated was carefully washed free from excess thiourea by means of alcohol; it was lemon yellow. The reaction proceeded according to the equation:



	Found %: Pt 34.16, 33.69; Cl 12.90, N 18.68
$4\text{Thio}_4\text{PtCl}_2$	Calculated %: Pt 34.23, Cl 12.43, N 19.03

The salt is of good solubility in water, and its aqueous solution, acidified with nitric acid, gives an immediate precipitate of silver chloride with silver nitrate. Thus, in compounds in which diallylamine does not form a ring, treatment with urea leads to complete elimination of diallylamine from the inner sphere.

c) Reaction with caustic alkali and cyclization.

If the dry salt HDCl_3Pt is treated with 5% NaOH and the mixture is heated on a water bath, cyclization of the diallylamine group occurs with formation of dichloro(diallylamine) platinum DCl_2Pt . The performance of this reaction gives some difficulty. If the reaction mixture is heated until the monoammine has completely reacted,

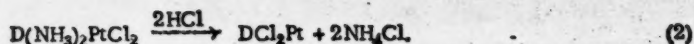
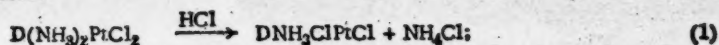
then part of the dichloro(diallylamine)platinum is converted into a hydroxo salt; otherwise, part of the monoammine remains unchanged and affects the analytical results:

Found %: Pt 52.89; Cl 21.08
 DCl_2Pt Calculated %: Pt 53.73; Cl 19.52
 In the original monoammine HDCl_2Pt %: Pt 48.83; Cl 26.61

Such are the properties of the compound obtained by the reaction between diallylamine and ammonium chloroplatinate (II) in neutral medium.

Action of hydrochloric acid on the mixed ammonia-diallylamine tetrammine $\text{D}(\text{NH}_3)_2\text{PtCl}_2$.

In view of the results of the investigations of the reaction of hydrochloric acid with dichloro(diallylamine)platinum, leading to the opening of the diallylamine ring, it was of interest to investigate the action of HCl on ammonia-diallylamine compounds, in particular $\text{D}(\text{NH}_3)_2\text{PtCl}_2$. Our experiments gave positive results, and it was established that, when hydrochloric acid reacts with the tetrammine $\text{D}(\text{NH}_3)_2\text{PtCl}_2$, one or two ammonia molecules, depending on the duration of heating only, are split off without disturbance of the ring. The resulting compounds are of the triammine and diammine series respectively: $\text{DNH}_3\text{ClPtCl}$ and DCl_2Pt . The respective reactions may be represented by the following equations:



The analytical results for the compound obtained by the first of these reactions are:

Found %: Pt 51.01, 50.86, 51.97; N 6.60, 7.41
 $\text{DNH}_3\text{ClPtCl}$ Calculated %: Pt 51.33 N 7.36

and for the compound obtained by the second reaction:

Found %: Pt 53.77, 53.66, 53.50; Cl 20.16, 20.44
 DCl_2Pt Calculated %: Pt 53.73 Cl 19.51

The two reactions are carried out by careful heating of the tetrammine $\text{D}(\text{NH}_3)_2\text{PtCl}_2$ with hydrochloric acid. The first ammonia molecule splits off particularly readily, possibly because this ammonia molecule is trans to the double bond.

II. Reaction of Diallylamine with Ammonium or Potassium Chloroplatinate (II) in Acid Medium and the Preparation of Monoammine II HDCl_2Pt .

The action of diallylamine on potassium chloroplatinate (II) in neutral medium does not lead to the isolation of any definite compounds. When diallylamine was added to an acidified solution of ammonium chloroplatinate (II) [0.5 g $(\text{NH}_4)_2\text{PtCl}_4 + 4 \text{ ml H}_2\text{O} + 2 \text{ ml conc. HCl}$], a bright yellow salt formed after about a day. Crystal-optical analysis indicated that the salt was homogeneous.

Found %: Pt 48.48; Cl 26.53; N 4.14

Ratio Cl/Pt = 3, N/Pt = 1.

The reaction between diallylamine and potassium chloroplatinate (II) in acid medium went in a completely similar fashion. The precipitate was bright yellow and contained 48.83% Pt, 26.77% Cl and 3.99% N. Again, Cl/Pt = 3, N/Pt = 1.

By a comparison of these results with the results of the analysis of the salt HDCl_2Pt , obtained by splitting dichloro(diallylamine)platinum with hydrochloric acid, we concluded that in this case a monoammine HDCl_2Pt was formed; this we indicated by the figure II, having in view the method by which it was prepared. We were confirmed in this view also by a comparison of the refractive indices of the two salts. Thus, for monoammine HDCl_2Pt (I): $n_D^{20} 1.765$; $n_D^{25} 1.680$; and for monoammine HDCl_2Pt (II): $n_D^{20} 1.767$; $n_D^{25} 1.680$.

Monoammine II gave the same inner-sphere substitution reactions as monoammine I. For comparison we give the results of the corresponding experiments: a) the reaction with ammonia proceeded in completely analogous fashion, the salt obtained being isolated as chloroplatinate (II), in which was found Pt 57.77% and N 8.14%; b) with thiourea under the same conditions a lemon-yellow salt, containing 34.16% Pt, was formed; c) with a 5% solution of caustic soda a dark yellow salt, containing Pt 53.38% Cl 18.68% was obtained.

Hence it may be concluded that both in the splitting of dichloro(diallylamine)platinum DCl_2Pt with hydrochloric acid and in the reaction between diallylamine and ammonium or potassium chloroplatinate (II) in acid medium, the same compound, the monoamine HDCl_3Pt , is formed.

The experimentally observed fact that ammonium chloroplatinate (II) and potassium chloroplatinate (II) react differently with diallylamine in acid medium deserves particular attention.

SUMMARY

1. The action of diallylamine on ammonium chloroplatinate (II) in neutral medium has been studied, and it has been shown that the monomer DCl_2Pt and the dimer $[\text{D}_2\text{Pt}][\text{PtCl}_4]$ are formed. In these compounds diallylamine occupies two coordination positions and forms a ring.
2. The view is expressed that diallylamine, in forming a ring with the platinum, unites through the nitrogen of the NH group and the double bond.
3. It has been shown that thiourea reacts with DCl_2Pt with formation of $\text{DThio}_2\text{PtCl}_2$, so confirming the stability of the diallylamine ring. The preparation of mixed ammonia-diallylamine compounds is also an indication of the stability of the diallylamine ring.
4. The action of concentrated HCl on DCl_2Pt has been studied, and it has been shown that the ring may be opened with formation of the compound HDCl_3Pt , in which diallylamine occupies one coordination position. A study of the reaction of this compound with thiourea has shown that diallylamine, when occupying one coordination position, is readily eliminated from the inner sphere with formation of the compound $\text{Thio}_2\text{PtCl}_2$.
5. The reaction of diallylamine with chloroplatinates (II) in acid medium has been studied. It has been shown that a compound HDCl_3Pt is obtained which is identical with the compound HDCl_3Pt obtained by boiling DCl_2Pt with concentrated HCl.
6. The reaction conditions have been found under which the re-closure of the ring occurs in the compound HDCl_3Pt .

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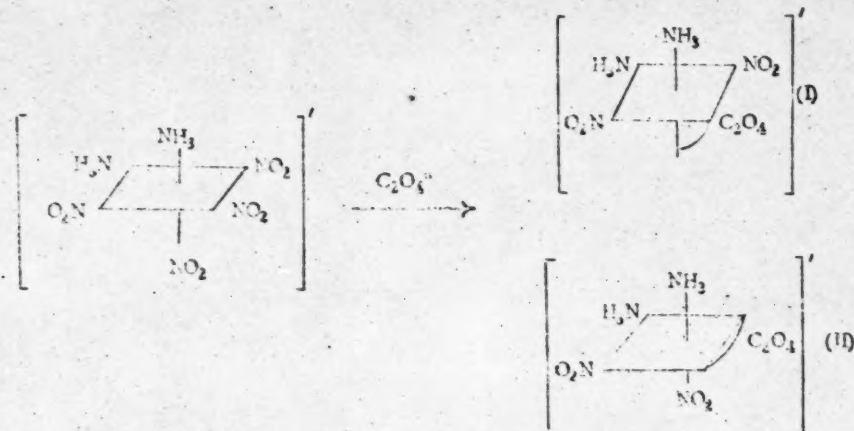
STRUCTURE OF THE COMPLEX ION $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$

G. B. Boky and E. A. Gilinskaya

According to coordination theory the ion $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ should exist in two forms, cis and trans. However, only one isomer is known. There is the contradictory evidence concerning the structure of this ion. The following facts support the cis configuration:

1) The absorption spectrum of $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ in the visible and ultraviolet regions consists of three characteristic bands. The same sort of absorption, with the same number and position of bands, is shown by trans-dinitrotetramminecobalt (II) chloride, whereas for the cis-dinitrotetrammine chloride the third band is absent. The third band disappears also for the compound $\text{NH}_4[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4(\text{NO}_2)_2]$, which is obtained from $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ by reaction with oxalic acid. A comparison of the spectra of these four compounds [1] has led to the conclusion that the presence of the third band is caused by the coordinate linkage $\text{NO}_2-\text{Co}-\text{NO}_2$, and that in the compound $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ only two NO_2 groups are in a trans position.

2) By the action of oxalic acid, two isomers of the compound $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4(\text{NO}_2)_2]$ have been obtained [2], one of which is resolved by strychnine into enantiomorphs. This fact is readily explained by a cis structure in the complex:



The isomer II, having an asymmetric structure, is capable of being resolved into enantiomorphs.

The following facts support the trans configuration:

1) Reaction with ethylenediamine [3] gave $[\text{Co}(\text{NO}_2)_4(\text{NH}_2)_2\text{Et}]$ as sole product. If the structure had been cis, the ethylenediamine would have eliminated the two adjacent NH_3 molecules. 2) In spite of a number of attempts, it was not found possible to resolve dioxalato substituted tetraamminecobaltate (II) into enantiomorphs [3], thus indicating a symmetrical structure for the dioxalato compound; an asymmetric dioxalato compound should have been obtained if the NH_3 groups had cis relationship in the tetraamminecobaltate. 3) An investigation [4] and comparison of the absorption spectra of a number of nitro isomers of tetraamminecobalt in the region 320-350 mμ (second spectral band) led to the conclusion, when the degrees of absorption and the position of the absorption maxima were taken into consideration, that the ion $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ contains two $\text{NO}_2-\text{Co}-\text{NO}_2$ bonds. 4) X-Ray structure investigation of $\text{Ag}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ [5] has established the trans configuration in the crystals of this compound.

The contradictory data concerning the structure of the ion $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ led Chernovoy in 1927 to suggest [6] that some investigators were working with one isomer, and some with the other. However, this suggestion is disproved by the consistency of the geometric constants cited by the authors of both groups of investigations.

Only the earliest investigations (through 1923) have been critically reviewed in the literature, and for some reason or other the last two investigations pointing to the trans position of the NH_3 groups in the complex $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ have passed unnoticed. Analysis of the earlier results led to a preference for the cis hypothesis, for the proof of the trans structure was acknowledged to be unconvincing. Thus, the course of the reaction with

ethylenediamine is explained by Grinberg [7] by the mobility of the adjacent groups NH_2 and NO_2 in the complex of the cis isomer, and it was possible to explain the lack of success in resolving the dioxalato derivative by imperfect technique [8]. This point of view, i.e., acceptance of the proof for the cis structure as satisfactory, is maintained by the authors of several chemical reference books [8] and also by the authors of recently published monographs on the structure of complex compounds [7,9].

Thus, the view acknowledging the cis configuration for tetranitro diammine-cobaltate [III] has become accepted in the chemistry of complex compounds. The appearance of further work, spectral and, particularly, X-ray [5], compels us, however, to treat this conclusion critically and to analyze the proof of the cis structure for the complex $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$. It is sufficient to consider the fact that these assertions are based on the properties of compounds of the type $\text{Me}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2\text{C}_2\text{O}_4]$, which are prepared from the tetranitrodiammine by reaction with oxalic acid. It is assumed that inner-sphere rearrangement during the reaction does not occur, although this supposition has never been verified for compounds of this type. The opposite hypothesis of isomerization of the complex under the action of oxalic acid makes the existence of the contradictory evidence concerning the structure of the complex ion $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ understandable.

The soundness of this hypothesis depends on the conclusiveness of the facts cited in favor of a trans structure for the complex. The nonconclusiveness of the first two proofs has been reviewed above. As regards the spectral work of 1937 [4], it has the defect of resting on the comparative method, which permits conclusions to be drawn only on the basis of analogies in absorption spectra. The most trustworthy method of investigation in the given case appears to be the X-ray-structure method. An X-ray investigation of $\text{Ag}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ [5] has shown that the complex has a trans structure, but analysis of this work shows that the author took the presupposed trans model of the complex as basis and did not examine all the possible arrangements of atoms in the crystal lattice. Hence, in order to determine the structure of the complex $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$, we have undertaken a verification of the structural type of $\text{Ag}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ and have determined the structural type of $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$.

EXPERIMENTAL

I. Repeat Determination of the Structural Type of $\text{Ag}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$

The compound $\text{Ag}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ was prepared from the analogous ammonium salt by double decomposition. It was found possible by crystallization to obtain only very fine crystals of octahedral or tabular habit (according to the rate at which the supersaturated solution was cooled). The goniometric and optical properties of the crystals were identical. Optical constants: $N_m > 1.782$; $N_p = 1.665$; indicatrix negative. Symmetry of external form from goniometric measurements: 4/mmm; goniometric $c/a = 1.495$.

TABLE

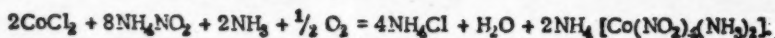
Distance	Wells' results	Our results
$\text{Co}-\text{N}(\text{NH}_3)$	2.30	1.95 ± 0.03
$\text{Co}-\text{N}(\text{NO}_2)$	1.92	1.96 ± 0.03
$\text{N}-\text{O}$	1.25	1.25 ± 0.05
$\text{O}-\text{O}$	2.08	2.15 ± 0.05

By the aid of X-ray photographs and by harmonic analysis of the reflection intensities, the structural type assigned by Wells was confirmed. The structure may be described as the closest possible packing of the complex ions $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$, the Ag^+ ions being disposed in the empty octahedral spaces of the structure. The compound is the trans isomer. The fundamental X-ray constants are $a = 6.95$; $c = 10.45$; $c/a_{(\text{X-ray})} = 1.490$. Fedorov symmetry group $D_{2h} = P4/mnc$. The five structural parameters:

$u(\text{zNH}_3) = 0.187$; $v(\text{xN}) = 0.200$; $x_0 = 0.305$; $y_0 = 0.225$; $z_0 = 0.096$. The interatomic distances in the complex are given in the table.

II. Determination of the Structural Type of $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$

The compound $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ was prepared by the usual method, which is based on the reaction:



The analogous potassium and thallium salts were obtained by double decomposition. Crystals of the three salts were measured on the goniometer. Refractive indices were determined by the immersion method in white light and also, for $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$, in monochromatic light. The crystals were found to have a symmetry of 222, whereas they are described in the literature as rhombodipyramidal (mmm). The refractive indices of $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ in white light are $N_g = 1.752$; $N_m = 1.716$; $N_p = 1.708$. The experimentally found refractive indices are compared by the method proposed in 1948 by Boky [10] with calculated values, and it was found that they corresponded most closely with the values calculated on the assumption of the trans configuration for the

complex. Peculiarities in the orientation of the optical indicatrix in $K[Co(NO_2)_4(NH_3)_2]$ and $Ag[Co(NO_2)_4(NH_3)_2]$ crystals led to a limitation of the possible positions of the complex in the lattice.

	X-ray Constants			
	a	b	c	v
$K[Co(NO_2)_4(NH_3)_2]$	11.27	12.76	6.72	964
$NH_4[Co(NO_2)_4(NH_3)_2]$	11.43	12.92	6.73	986

Fedorov symmetry group $D_2^4 = P2_12_12_1$

By a combination of harmonic analysis of X-ray interference intensities with geometric analysis by the aid of space models the structure variant corresponding most closely to the experimental results was found. In the structure so found the NH_3 groups are trans to one another.

The structure of $K[Co(NO_2)_4(NH_3)_2]$ is close to that of $Ag[Co(NO_2)_4(NH_3)_2]$. Replacement of Ag atoms in the latter compound by potassium atoms leads to the following distortions in the lattice of $Ag[Co(NO_2)_4(NH_3)_2]$: 1) increase in the parameter "a" from 10.4 to 11.2; disturbance of the coplanarity of the layers; 3) conversion of the octahedral coordination polyhedron of the Ag atom into a trigonal prism around the K atom. The peculiarities of the structure explain some of the physical properties of the crystals: the orientation of the optical indicatrix and the perfect [110] prism cleavage of the crystals.

The direct X-ray method of analysis shows, in contradiction to the chemical methods, that the complex ion $[Co(NO_2)_4(NH_3)_2]^-$ has the trans configuration. This fact shows that in those cases in which the probability of inner-sphere rearrangements is great (in the compounds of elements having complex-forming properties poorer than those of platinum) it is essential when determining structure to have recourse to physical methods, particularly X-ray structural analysis.

SUMMARY

1. For the first time, the crystal-optical method has been used for determining the structure of a complex ion; it led to the conclusion that the ion $[Co(NO_2)_4(NH_3)_2]^-$ has the trans configuration.

2. The trans configuration of the complex ion has been proved also by direct X-ray structural analysis of the compounds $Ag[Co(NO_2)_4(NH_3)_2]$ and $K[Co(NO_2)_4(NH_3)_2]$, which belong to different structural types.

3. The fact that the NH_3 groups are in cis positions in the ion $[Co(NO_2)_2C_2O_4(NH_3)_2]^{2-}$ [2] proves, when our results concerning the trans structure of the tetranitrodiamminecobaltate (III) from which it is derived are taken into account, that, under the influence of the oxalate ion in solution, a rearrangement of substituents of the complex occurs. The probability of such rearrangements for cobalt complex compounds (and other atoms having not very powerful complex-forming properties) is evidently greater than is usually supposed. Consequently, the role and significance of direct physical methods for the determination of the structures of complex compounds is increased.

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HYDRATION OF IONS IN AQUEOUS SOLUTION

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The determining significance of the interaction between solute and solvent for the properties of solutions was first pointed out by Mendeleev. Mendeleev was also the first to point out the necessity for the development of a theory of the liquid state as a prerequisite of the study of solutions [1]. In the present paper the phenomenon of ion hydration in aqueous solutions is examined in its relation to existing data concerning the nature of the thermal agitation of the particles of the liquid and also in its relation to concepts concerning the structure of dilute aqueous solutions of electrolytes, based mainly on the study of the coordination numbers of ions in aqueous solutions.

In numerous investigations devoted to the question of ion hydration, the authors try to determine the number of water molecules bound to ions in solution—the so-called hydration numbers. However, the hydration numbers determined for particular ions from various properties of the solutions generally vary considerably among themselves. Ulich [2] and Darmon [3] in examining the phenomenon of ion hydration employ Stokes' law. Although the possibility of applying this law to the case of ionic movements in solution is subject to some doubt, it must nevertheless be considered that it permits an evaluation of quantities that are essential for the understanding of hydration. We shall examine the movement of an ion in an infinitely dilute aqueous solution. If Stokes' law is applicable

$$U\eta r = \text{const}, \quad (1)$$

where U is the electrochemical mobility of the ion in infinitely dilute solution at a certain temperature; η is the viscosity of the medium at the same temperature; and r is the ionic radius. If the viscosity is measured in poises and ionic radii in Angstroms, then the numerical value of the constant is 0.820 Z , where Z is the ionic charge. The constant is independent of temperature.

If in Equation 1 we substitute the values of ionic mobility found experimentally and take the viscosity of the medium to be that of pure water, then the equation gives values for the ionic radii (r_s) which are in general different from the crystallographic values (r_c). These radii are called Stokes radii. A collection of data on the Stokes radii of a large number of ions is given by Darmon [3].

If for any ion $r_s > r_c$, it is assumed that the ion is hydrated in aqueous solution; if $r_s < r_c$, it is assumed that the ion is not hydrated. Darmon and Ulich determined hydration numbers from the excess of the Stokes ionic volumes over the crystallographic volumes. As is known, it is usual to explain the increase in a series such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , in the electrochemical mobility of ions by the diminution in the series in Stokes radius. It appears, however, that such an approach does not correspond to the nature of the phenomenon of ion hydration in solutions.

Darmon [3] drew attention to the fact that temperature coefficients for the mobilities of hydrating ions (e.g. at 18°) are greater, and those of nonhydrating ions are less, than the absolute value of the temperature coefficient of the viscosity of water at the same temperature. However, it would appear to follow from Equation (1) that

$$\frac{1}{U} \frac{dU}{dT} = - \frac{1}{\eta} \frac{d\eta}{dT}.$$

For hydrating ions Darmon explains this difference as due to dehydration, occurring as the temperature rises, which will lead to a reduction in the Stokes radius. Actually, in that case

$$\frac{1}{U} \frac{dU}{dT} = - \frac{1}{\eta} \frac{d\eta}{dT} - \frac{1}{r_s} \frac{dr_s}{dT}.$$

in which $\frac{dr_s}{dT} < 0$. It is however difficult by this method to explain the difference between $\frac{1}{U} \frac{dU}{dT}$ and $-\frac{1}{\eta} \frac{d\eta}{dT}$ in the case of nonhydrating ions: it would have to be associated with $\frac{dr_s}{dT} > 0$.

The phenomenon of ionic hydration in aqueous solutions should be regarded from a different point of view, not having its origin in the concept of the binding by the ions of a particular number of water molecules.

A more general approach to the study of the state of ions in aqueous solutions should be developed. The elucidation of the question of the binding by the ions of this or that number of water molecules should arise from such an approach only in the form of a deduction. It is possible that a general approach of this kind could be found by an examination of the effect of the ions on the thermal, particularly translational, motions of the water molecules that are nearest to them in the solution*. It will be evident that fairly firm binding by the ions of any number of water molecules will be associated with a considerable enfeeblement of this movement.

Action of Ions on the Translatory Movement of Water Molecules

Interaction of ions with the nearest water molecules in the solution causes the potential energy of these molecules to differ from that of water molecules in water, and there is therefore a difference in the heights of the potential barriers around the temporary equilibrium positions of water molecules in the vicinity of ions and of those of water molecules in a purely "aqueous" environment. The action of ions on the viscosity of water stands in direct relation to this. This action, as previously pointed out [5], consists in the change brought about by the ions in the activation energy of viscous flow of the water molecules that are the main constituents of the ionic environment in the change in the heights of the corresponding potential barriers. Thus it consists in the action of ions on the translatory movement of these molecules. It has been noted that ions affect the viscosity of water in different ways: small singly charged and multicharged ions increase the viscosity, and large single-charged ions reduce it. Consequently, ions act in different ways also on the translatory movement of the nearest water molecules. The small singly charged and multicharged ions (for example Li^+ , Mg^{2+} , Ca^{2+} , hydrating ions) enfeeble this movement: if τ_1 is the mean time occupied by water molecules in equilibrium positions in the coordination layer of an ion, and τ is the corresponding time for pure water, then for such ions $\tau_1 > \tau$. On the other hand, a number of ions (for example K^+ , Cs^+ , Cl^-) increase the translatory movement of the nearest water molecules. For such ions $\tau_1 < \tau$. Water molecules in their vicinity become more mobile than they are in pure water. This phenomenon has been called "negative hydration" [6]. Watari [7] came to a similar conclusion as a result of investigations into questions of diffusion in solutions of electrolytes.

This concept of the effect of ions on the translatory movement of the nearest water molecules is in accord with the dependence of the activity coefficient of water in solutions of electrolytes on concentration. It is readily shown that the enfeeblement of the translatory motion of water molecules (reduction in their potential energy, rise in the negative potential) must lead to reduction in the activity coefficient of water and, on the other hand, intensification of the translatory motion (increase in potential energy) must lead to an increase. It has been shown that whereas activity coefficients of water in solutions of electrolytes having hydrating cations are less than unity (with the exception of a short low-concentration range), the activity coefficients of water in the case of cations showing negative hydration (K^+ , Rb^+ , Cs^+) are greater than unity over a considerable range of concentration [8].

The concept of negative hydration is not contradictory to the fact that the hydration of ions is always accompanied by the evolution of fairly large amounts of energy (high heats of hydration for ions). Actually, the energy of hydration of an ion may be divided into two parts: that conditioned by interaction of the ion with water molecules of its environment, and that conditioned by interaction with the remaining molecules. The first part may be either a reduction or an increase (negative hydration) in energy. However, the second part is always a reduction occurring in the ion-water system during dissolution of the ion, i.e. it always corresponds to evolution of energy. Although the energy of the interaction of an ion with a separate water molecule that does not form part of its immediate environment is very small, the total energy summed over many molecules attains high values; a considerable part of the heat of hydration of the ion is associated with it [9,10]**.

* In accord with the concepts, now fairly firmly established, concerning the nature of the thermal movement of particles in liquids (particularly water molecules in water), it is considered that this movement consists of vibrations about certain temporary positions of equilibrium and intermittent jumps from one equilibrium position to another, neighboring one (translatory movement) [4]. At a given temperature the translatory movement depends on the heights of the potential barriers surrounding the temporary equilibrium positions of the particles; it is characterized by the mean time occupied by a particle around one equilibrium position. In the present paper an examination is made of the translatory movement of water molecules relative to ions, which is characterized by the mean time occupied by water molecules in temporary equilibrium positions in the coordination layer of the ion.

** This follows from the calculations of Moelwyn-Hughes [10] on heats of ionic hydration if it is assumed that the coordination number for all ions in aqueous solutions is 4, which, according to the author, gives results that are just as satisfactory as the value of 6 that he assumes.

In order to make a quantitative examination of the effect of ions on the translatory motion of the nearest water molecules it is necessary to evaluate, at least approximately, the ratio τ_i/r for individual ions.* If the height of the potential barrier surrounding the temporary equilibrium positions of water molecules in water is $\frac{E}{RT}$ (per mole of water), then $\tau = \tau_0 \cdot e^{\frac{E}{RT}}$ [4]. If the ion changes the value of E to $E + \Delta E$, then in the vicinity of such an ion

$$\tau_i = \tau_0 \cdot e^{\frac{E + \Delta E}{RT}} = \tau_0 \cdot e^{\frac{\Delta E}{RT}}$$

and therefore

$$\frac{\tau_i}{\tau} = e^{\frac{\Delta E}{RT}} \quad (2)$$

Hence, in order to evaluate the ratio $\frac{\tau_i}{\tau}$, it is sufficient to evaluate the value of ΔE , the change produced by the ions in the potential barrier surrounding the temporary equilibrium positions of water molecules, or the change in the activation energy of viscous flow for these molecules. For the evaluation of ΔE , Stoke's law may be used.

The resistance experienced by an ion in moving in the solution is determined mainly by the activation energy of viscous flow of the water molecules immediately surrounding the ion. In this connection, η in Equation (1) must be understood as the viscosity of the water in the immediate vicinity of the ion and will have some value η_i that differs from the viscosity of pure water. The quantity of η_i is evidently the viscosity that water would have if the activation energy of the viscous flow of its molecules were the same as that of molecules comprising the immediate environment of an ion. The quantity r must be taken as the crystallographical radius of the ion (r_c). Equation (1) may then be written:

$$U \eta_i r_c = \text{const}; \quad (1')$$

and it permits η_i to be found (we note that $\frac{\eta_i}{\eta} = \frac{r_s}{r_c}$). The viscosity is related to the activation energy of viscous flow of molecules (E per mole) by the formula of exponential form, $\eta = A e^{\frac{E}{RT}}$. Hence, approximately,

$$\eta_i = A e^{\frac{E + \Delta E}{RT}}$$

and

$$\frac{\eta_i}{\eta} = e^{\frac{\Delta E}{RT}} \quad (3)$$

(η is the viscosity of pure water). Comparing Equations 3 and 2, we see that

$$\frac{\tau_i}{\tau} = \frac{\eta_i}{\eta} \quad (4)$$

Having determined η_i from Equation (1'), it is possible with the aid of Equation (3) to evaluate the value of ΔE for various ions: $\Delta E = RT \ln \eta_i/\eta$. Thus for the ions Li^+ , Na^+ , K^+ , and Cl^- , ΔE has the respective values of +0.6, +0.3, -0.1, and -0.2 kcal/mole of water.

In order to evaluate ΔE , use may also be made of experimental data on temperature coefficients of electrochemical ionic mobility. It is then necessary to postulate that the ionic radius in solution has the crystallographic value and that Stokes' law may be applied to the movement of ions in solution. It is sufficient to suppose that r is independent of temperature and that the coefficient of friction for movement of the ion is expressed by the formula $F = \eta \varphi(r)$, where φ is any function of r that is independent of temperature. As shown previously [6], the following relation is then obtained between the temperature coefficients of ionic mobility and the viscosity of water:

$$\frac{1}{U} \frac{dU}{dT} = - \frac{1}{\eta} \frac{d\eta}{dT} + \frac{\Delta E}{RT^2} \quad (5)$$

* In the present work, singly charged ions are examined.

Equation (5) permits, among other things, a very simple interpretation of the difference (Darmois [3]) between $\frac{1}{U} \frac{dU}{dT}$ and $-\frac{1}{\eta} \frac{d\eta}{dT}$, which was referred to at the beginning of this paper. Actually, if $\Delta E > 0$ (hydrating ions), then $\frac{1}{U} \frac{dU}{dT} > -\frac{1}{\eta} \frac{d\eta}{dT}$, and if $\Delta E < 0$ (negative hydration), then $\frac{1}{U} \frac{dU}{dT} < -\frac{1}{\eta} \frac{d\eta}{dT}$.

An approximate evaluation of ΔE by Equation (5) for various ions gives, for example for Li^+ and Cl^- [6], the values $\Delta E_{\text{Li}^+} \approx 0.4$ kcal/mole of water and $\Delta E_{\text{Cl}^-} \approx -0.4$ kcal/mole of water. Thus, the evaluation of ΔE by the two methods described yields fairly close values. In any case it may be concluded that a correct indication of the order of ΔE is given.

By the use of these evaluations of ΔE , or simply by the aid of Equation (4), the ratio $\frac{\tau_1}{\tau}$ may be determined for various ions. For K^+ and Cl^- τ_1 is about 0.9τ and 0.6τ respectively, and for Li^+ and Na^+ it is 3.0τ and 1.8τ respectively.* The value of τ_1/τ is evidently a quantitative expression of the "binding" by the ions of the nearest water molecules in the solution. It should be noted that it is doubtful whether it is possible to speak of permanent hydration in the case of dissolved ions**. Rejection of the concept of permanent hydration is characteristic of the approach to the treatment of specific heats of ions in aqueous solution developed in the work of Kapustinsky [11].

As already noted, in the study of the state of ions in aqueous solutions, great importance is to be attached to the coordination numbers of ions in solutions—the mean numbers of constantly interchanging water molecules that comprise the immediate environments of ions in aqueous solutions. It has been established that the coordination numbers of ions in dilute aqueous solutions are close to the mean coordination number of water molecules in water [12,13]. It follows that the structure of water itself has a determining significance in the formation by water molecules of the equilibrium environment of ions in solution, which is undoubtedly related to the dynamic nature of this environment (constant exchange of water molecules around the ions). The extremely great importance of the structure of water in the phenomenon of ion hydration in aqueous solution is emphasized by the existing data on the temperature dependence of the integral heats of solution of electrolytes [14,15].

Although the coordination numbers of ions in dilute aqueous solutions approximate to four, the density of the distribution of water molecules around ions is different for different ions (the sizes of the ions differ). It has been shown previously that this density characterizes the hydration of individual ions in solution [12].

Dividing Line between Hydrating and Nonhydrating Singly Charged Ions

The difference between the potential barriers surrounding the temporary equilibrium positions of water molecules in water and those in the vicinity of ions is related to the change produced by the ions in the potential energy of the nearest water molecules. It is clear that the raising of potential barriers ($\Delta E > 0$) is peculiar to ions that reduce the potential energy of the nearest molecules (increase their negative potential); on the other hand, the case $\Delta E < 0$ (negative hydration) corresponds to increase in the potential energy of the nearest molecules.

The change produced by ions in the potential energy of the nearest water molecules may be treated by the aid of the concept of the structure of dilute aqueous solutions of electrolytes based on estimations of the coordination numbers of ions in solutions [13]. When this is done it is found that there is a fundamental dividing line between hydrating and nonhydrating singly charged ions, i.e., a certain limiting value of the crystallographic ionic radius such that singly charged ions having radius less than this value are hydrating ions (reduce the potential energy of the nearest water molecules), and those having radius greater than this value are nonhydrating ions (increase the potential energy of the nearest molecules).

Bernal and Fowler [16] in an examination of this question start from the following considerations: the water molecule in water has four immediate neighbors, whereas the water molecule in the coordination layer of the ion has three immediate neighbors—the ion and two water molecules (cations are under consideration). Consequently, true hydration, i.e., reduction by the ions of the potential energy of the nearest water molecules, occurs, according to Bernal and Fowler, when the reduction in the potential energy of a water molecule caused by an ion is greater than the reduction caused by two water molecules.

* It may be noted that τ is of the order of 10^{-10} second.

** It has already been noted [6] that rejection of the concept of permanent hydration does not contradict the results of experiments on the transfer of water by ions during electrolysis.

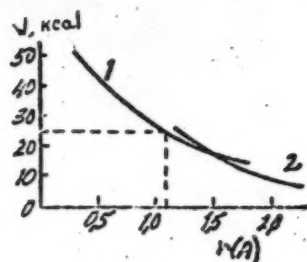
TABLE

Crystallographic radii, ΔE and $\frac{r_1}{r}$
for singly charged ions *

Ion	$r_c(\text{\AA})$	ΔE (kcal)	$\frac{r_1}{r}$
Li^+	0.78	+ 0.6 ₃	3.8
Na^+	0.98	+ 0.3 ₄	1.8
Ag^+	1.15	+ 0.1 ₄	1.3
K^+	1.33	- 0.0 ₇	0.8 ₉
Ti^+	1.50	- 0.1 ₅	0.7 ₇
Cs^+	1.65	- 0.2 ₄	0.6 ₈
Cl^-	1.81	- 0.2 ₅	0.6 ₅
Br^-	1.96	- 0.3 ₃	0.5 ₉
I^-	2.20	- 0.3 ₇	0.5 ₃

Inasmuch as it has been established that the coordination numbers of ions in dilute aqueous solutions approximate to four [12], it is possible to give a treatment of the effect of ions on the potential energy of the nearest molecules of water in the solution by placing the ion in one of the "coordination positions" in the structure of water. In so doing, the difference in radius between the ions and water molecules may be neglected, mainly because in the region that is of interest (near to the limiting value of the radius that divides singly charged ions into hydrating and nonhydrating) this difference is small.

Replacement in the water structure of a water molecule by an ion without reorientation of the nearest



Dependence of the electrostatic energy of the interaction of ions with molecules oriented by them on the ionic radius: 1) cations; 2) anions.

molecules can lead only to an increase in the potential energy of these molecules. Actually, the orientation of water molecules in the water structure relative to a coordination position that is occupied by an ion is such that the change, due to interaction with the ion, in the potential energy of the water molecules that are nearest to the ion is on the average zero: the four molecules are oriented in pairs relative to the ion by means of their opposite poles.

However, the fact that the ion occupies a coordination position in the water structure leads to absence in the water molecules nearest to the ion of one of the four $\text{H}_2\text{O}-\text{H}_2\text{O}$ bonds. If the energy of this bond is e kcal/mole, then owing to the introduction of the ion the potential energy of its nearest water molecules (if they are reorientated by the ion) will be increased by e kcal.

The molecule that is nearest to the ion has four neighbors — the ion, and three water molecules not entering into the immediate environment of the ion, with which it is bound by three bonds of energy e . Hence the reorientation of such a molecule by the ion leading to the rupture of these three bonds will evidently occur if $W > 3e$. However, this is still insufficient to cause the ion to reduce the potential energy of the nearest water molecules: the reduction in potential energy during reorientation must be greater than e (the increase in potential energy associated with the fact that the adjacent coordination position

* The values of ΔE and r_1/r refer to 18°. The second significant figure in these values is mainly of calculation significance.

** In any case the mean is small and may be taken as equal to zero.

The considerations here advanced may be illustrated by a much simplified scheme for the replacement of the water molecule in the water structure by an ion: a greatly simplified picture of the arrangement of molecules in water may be represented in a plane in the form of circles in contact arranged so that every circle touches four others (arranged, for example, at the intersections of a square-mesh net). The poles of the water molecules must be arranged so that unlike poles are in contact. One circle is to be taken as the ion. Such a scheme (Footnote continued on next page)

in the water structure is occupied by an ion), i.e. we must have

$$W - 3e > e \text{ or } W > 4e.$$

This value of W defines the boundary between ions that reduce and ions that increase the potential energy of the nearest water molecules (between hydrating and nonhydrating ions). In the range $4e > W > 3e$ there is reorientation by the ions of the nearest water molecules, but the ions increase the potential energy of these molecules. When $W < 3e$ the ions increase the potential energy of the nearest water molecules and do not reorient them.

The dependence of the energy W on the crystallographic radius of the ion is represented by the curve shown in the figure. The energy of the bond H_2O-H_2O in water (e), according to Eley and Evans [9], is approximately 5.2 kcal/mole ($6.2 + 4.2/2$; only electrostatic interaction is considered). According to Pople [17], the most rigorous treatment of the electrostatic energy of the H_2O-H_2O bond in water gives 6.0 kcal/mole. We shall assume that e is 6.0 kcal/mole. The dividing line between hydrating and nonhydrating ions is then determined by a value of W of $6 \cdot 4 = 24$ kcal. On the $W(r)$ curve a value of $r = 1.1$ Å corresponds to this value of W .

The limiting value obtained for the radius agrees in general with the results of the examination of the effect of ions on the translatory motion of the nearest water molecules, as can be seen from the table. It is confirmed also by values of the temperature coefficients of electrochemical mobility for singly charged ions:

$$\frac{1}{U} \frac{dU}{dT} > -\frac{1}{\eta} \frac{d\eta}{dT} \text{ for } Li^+ \text{ and } Na^+ (\eta \text{ is the viscosity of water}).$$

$$\frac{1}{U} \frac{dU}{dT} < -\frac{1}{\eta} \frac{d\eta}{dT} \text{ for } K^+, Cs^+, Cl^-, Br^- \text{ and } I^-.$$

The range $4e > W > 3e$ corresponds to range of ionic radii from 1.1 to 1.5 Å. It should be noted that e and $W(r)$ are in the nature of evaluations.

SUMMARY

1. The effect of ions in aqueous solutions on the translatory motion of the nearest water molecules has been examined. Ions such as Mg^{2+} , Ca^{2+} , Li^+ , and Na^+ reduce this motion ($r_i > r$). A number of ions (for example, K^+ , Cs^+ , Cl^-) increase it ($r_i < r$).
2. It has been shown that the mean period occupied by molecules of water in temporary equilibrium positions near to Li^+ and Na^+ ions is approximately 3.0τ and 1.8τ ; the values near to K^+ and Cl^- are 0.9τ and 0.6τ .
3. It has been shown that there is a certain limiting value for the crystallographic radius which divides singly charged ions into hydrating and nonhydrating.
4. The structure of water is of highly fundamental significance in the phenomenon of ion hydration in dilute aqueous solutions.

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(continuation of footnote from previous page) represents the replacement of a water molecule by an ion without reorientation of the nearest molecules. It is not really correct, but it is probable that it gives a correct rendering of the peculiarities that are fundamental to the considerations advanced.

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DETERMINATION OF THE DISTRIBUTION COEFFICIENTS OF RADIUM AND OF ITS ISOTOPE ThX BETWEEN MELT AND CRYSTALS OF CALCIUM NITRATE

V. G. Khlopina, V. R. Klokman, and E. G. Pekelnaya

The anhydrous nitrates of calcium, strontium, barium, and lead, which crystallize in the form of regular octahedra, form, as is well known, an isomorphous group.

The distribution coefficient of radium in the crystallization of the solid phase from aqueous solution has been determined for only three members of this group, the nitrates of barium [1], strontium [2] and lead [3]. In all three cases the distribution coefficient D was found to be less than unity, which indicates that enrichment in the micro component occurs in the solid phase, for the distribution coefficient D is an expression of the number of times that the separating crystals are richer in micro component than the salt remaining in the solution:

$$D = \frac{x(100-y)}{y(100-x)}$$

where x and $(100-x)$ are the percentage amounts of radio element going into the crystals and remaining in the solution (or melt), respectively, and y and $(100-y)$ are the percentage amounts of the isomorphous salt going into the crystals and remaining in the solution (or melt), respectively.

The distribution coefficient has not been determined for calcium nitrate, because it crystallizes from aqueous solutions in the form of the tetrahydrate, which forms monoclinic crystals that are not isomorphous with anhydrous radium nitrate crystals. From the melt, however, calcium nitrate crystallizes as the anhydrous salt, isomorphous with radium nitrate, and so in this case the distribution coefficient of radium can be determined also for this fourth member of the isomorphous group.

The distribution coefficients of radium between melt and crystals were determined by us for the other three isomorphous salts in one of our previous investigations [4].

EXPERIMENTAL

In this work we used the method that we had already developed [4]. We studied the distribution coefficient of radium between melt and calcium nitrate crystals in the system $\text{Ca}(\text{NO}_3)_2\text{--Ra}(\text{NO}_3)_2\text{--Na}(\text{NO}_3)_2$.

Anhydrous calcium nitrate was prepared by drying the tetrahydrate carefully at 150° . Sodium nitrate was dried at the same temperature. As distributing micro component we used radium and its isotope ThX, the latter being prepared by collection of emitted atoms on a negatively charged plate. The activity of the melt before and after separation of the solid phase, which was required for the determination of the percent radium that had passed into the solid phase, was measured by the emanation method.

Before carrying out the distribution experiments, the melting curve of the $\text{Ca}(\text{NO}_3)_2\text{--NaNO}_3$ system was determined. Measurements were made for up to 70 mol. % of calcium nitrate: mixtures of greater calcium nitrate content begin to become opalescent, and the determination becomes inexact. According to our results, the eutectic melting point of this system is 230° and corresponds to 49.5 mol. % of calcium nitrate. Menezies and Dutt [5] give the eutectic temperature as 236° and the eutectic composition as 50 mol. % of calcium nitrate.

From the melting curve of the system the amount of separated solid phase $[\text{Ca}(\text{NO}_3)_2]$ was calculated; so also were the compositions of the initial and final melts. The results of the experiments on the determination of the distribution coefficient of radium between melt and crystals of calcium nitrate are given in Table 1.

In Experiments 4 and 9 ThX was taken as micro component; in the remaining experiments, radium was taken. The experiments were carried out without stirring, for it has been shown that the rate of attainment of equilibrium for the case of the separation of a solid phase is independent of whether or not the melt is stirred [6]. Experiments 9 and 10 were carried out by the method of recrystallization of an excess of calcium nitrate in a

TABLE 1

Distribution of Ra between Melt and Crystals of $\text{Ca}(\text{NO}_3)_2$

Expt. No.	Amt. of $\text{Ca}(\text{NO}_3)_2$ crystallized out (%)	Amt. of Ra transferred to solid phase (%)	D
1	30.0	27.0	0.9
2	40.0	36.5	0.9
3	40.0	35.4	0.8
4	45.0	45.4	1.0
5	52.3	56.2	1.1
6	52.3	56.7	1.2
7	52.3	53.4	1.0
8	52.3	55.4	1.2
9	64.0	63.7	1.0
10	74.3	74.9	1.0
Mean . . .			1.0

TABLE 3

Radii of Ions of Bivalent Metals

Element	Ionic radius R (Å)	$R_{\text{Ra}} - R_{\text{El}}$	Difference in radii (% of the lesser)
Ra	1.52	—	—
Ba	1.43	0.09	6
Sr	1.27	0.25	20
Ca	1.06	0.46	43
Pb	1.32	0.20	15

The first peculiarity is that radium forms mixed crystals most readily not with its closest neighbors in the group—barium and strontium—but with further removed elements—calcium and lead; i.e. in this isomorphous group the propensity for the formation of mixed crystals with radium among the analogous elements does not follow the same order as the ionic radii (see Table 3).

The second peculiarity is that, in the systems that we have studied so far in which radium is distributed between melt and crystals of isomorphous salts, enrichment in radium of the solid phase has not been observed.

SUMMARY

1. The distribution coefficient of radium and of its isotope ThX between melt and crystals of calcium nitrate has been determined.
2. It has been found that also in this system the distribution of radium between melt and crystals of an isomorphous salt does not lead to enrichment of the solid phase in radium.
3. It has been shown that in the isomorphous group of Ca, Sr, Ba, and Pb nitrates radium readily forms mixed crystals with the nitrates of calcium and lead, but not with those of strontium and barium, its closest neighbors in the group.

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TABLE 2

Distribution Coefficients of Radium between Melts and Crystals of Nitrates of Bivalent Metals

Isomorphous salt	D
$\text{Ba}(\text{NO}_3)_2$	0.4
$\text{Sr}(\text{NO}_3)_2$	0.4
$\text{Ca}(\text{NO}_3)_2$	1.0
$\text{Pb}(\text{NO}_3)_2$	1.0

melt of definite composition at a definite temperature over a period of four hours; this permitted an increase in the amount of solid phase separated, without rise in temperature. All the remaining experiments were carried out by the method of solid-phase separation from the saturated melt.

It will be seen from Table 1 that the distribution coefficient remains constant at the mean value

of unity, independently of the amount of solid phase separated. The amount of solid phase varied from 30 to 74.3%. From these and our previous results on the distribution coefficients of radium between the melt and crystals of isomorphous salts, we may construct the following composite table (Table 2) for all four members of this isomorphous group.

It will be seen from Table 2 that in the case of the distribution of radium between the melt and crystals of barium and strontium nitrates, the distribution coefficient D is 0.4, i.e. in this case there is enrichment of the micro component of the melt. For the distribution of radium between melt and crystals of calcium and lead nitrates, D is unity, which indicates uniform distribution of the micro component between melt and crystals for these salts. Thus, in the distribution of radium between melt and crystals for the isomorphous salts, two interesting peculiarities are to be observed.

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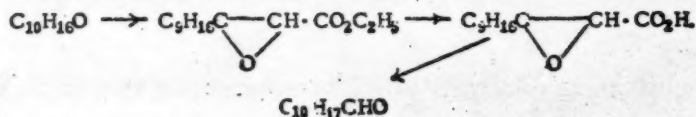
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β-AMINO ACIDS

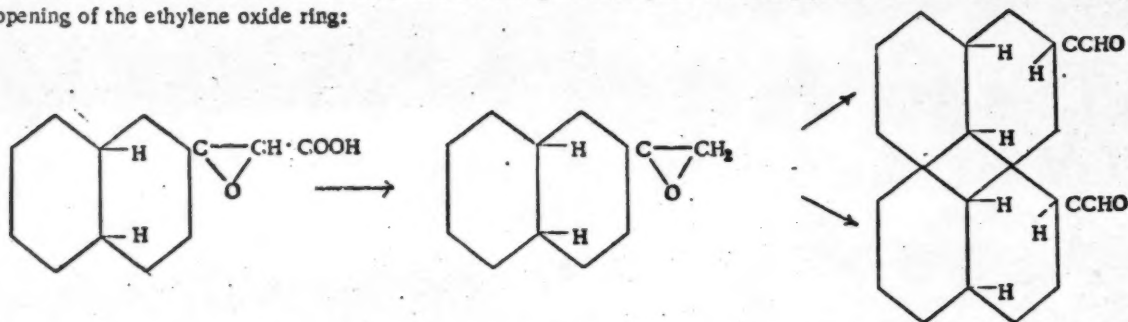
COMMUNICATION 34. SYNTHESIS AND CHARACTERIZATION OF β-AMINODECAHYDRO-2-NAPHTHALENE-PROPIONIC ACID

V. M. Rodionov and L. V. Antik

As starting material for the synthesis of β-(2-decalyl)-β-alanine (β-aminodecahydro-2-naphthalenepropionic acid), β-decalone (octahydro-2-(1H)-naphthalenone) was taken; this was obtained by oxidation of cis-β-decalol (cis-decahydro-2-naphthol), m.p. 105°. β-Decalone was condensed with ethyl chloroacetate by Darzens' method [1] to yield a glycidic ester, which on hydrolysis and decarboxylation gave decahydro-2-naphthaldehyde:



The synthesis of the β-decalyl-β-amino acid was brought about by condensation of the aldehyde with malonic acid according to the method of Rodionov and coworkers [2]; the yield of β-amino acid was about 50%, based on the amount of aldehyde taken for reaction. At the same time, a mixture of unsaturated acids of the β-decalylacrylic type was isolated. The syntheses and the purification of the substances obtained were rendered very difficult by the fact that in the reactions studied mixtures of difficultly separable stereoisomeric forms could arise. The formation of these were possible, evidently, because the decahydro-2-naphthaldehyde used was itself a mixture of two stereoisomeric forms, produced during decarboxylation of the glycidic acid and subsequent opening of the ethylene oxide ring:

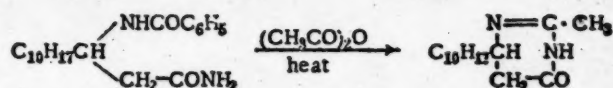


The present investigation is not concerned with this interesting reaction, which will be the subject of a future study.

The possibility of producing isomeric forms was noted already in the early stages of the work, but attempts to separate these forms, even by repeated tedious recrystallizations that greatly reduced the yields of the desired substances, were not always successful. The first successful separation of this sort was effected by the aid of acid chlorides of N-benzoyl derivatives of β-(2-decalyl)-β-alanine. The isomeric acid chlorides have different solubilities in ether, and the amides obtained from them are sharply distinguished by their melting points, 210-212° and 250 and 252°. Mixed melting point tests show depressions. The corresponding isomers of N-benzoyl-β-(2-decalyl)-β-alanine were prepared by cautious hydrolysis of the amides.

In order to characterize the new β-amino acids, attempts were made to synthesize their N-carbamoyl derivatives (the related ureido acids), related hydricuracils, and also, by the Curtius reaction, 3-benzoyl-4-(2-decalyl)-2-imidazolidinones and the corresponding decalylimidazolidinones. When carrying out the Curtius reaction it was again found possible, owing to the different solubilities of the benzoyldecalylimidazolidinones in benzene, to separate two isomers, m.p. 213-215° and 173.5-175°. The isomer of m.p. 213-215° gave 4-(2-decalyl)-2-imidazolidinone.

The transacylation reaction discovered previously in our laboratory, in which amides of benzoylated acids are heated with acetic anhydride [3], was carried out also on the amide of β -(2-decalyl)- β -alanine; instead of cyclization to 6-(2-decalyl)-5,6-dihydro-2-phenyl-4(3H)-pyrimidinone, the corresponding 2-methyl compound was isolated:



The ureido acid, hydouracil, hydrazide, and azide were obtained in good yields by the usual methods (see Experimental).

EXPERIMENTAL

Preparation of the Glycidic Ester. Finely ground sodamide (18.5 g) was introduced under mechanical stirring at 15–20° into a mixture of cis- β -decalone (octahydro-2(1H)-naphthalenone) (60 g) (prepared by oxidation of cis-decalol, m.p. 105°, with chromic acid), ethyl chloroacetate (48.5 g), and dry benzene (90 ml). After being stirred at this temperature for three hours, the reaction mixture was poured onto ice (280 g); the oil formed was separated, and the aqueous layer was extracted twice with benzene (100 ml each time). The benzene extract was mixed with the separated oil, and the mixture was washed carefully with water until it reacted neutral; it was then dried over sodium sulfate. Benzene was removed, and the residue was vacuum-distilled, yielding the glycidic ester (53.8 g, 57.3%), b.p. 178–191°/20 mm. At the same time, unchanged β -decalone (15.9 g, 26.5%) and a high-boiling (about 200°/20 mm), possibly polymeric substance (which was not investigated) (6.7 g) were isolated.

Found %: C 70.45; 70.66; H 9.37; 9.39
 $\text{C}_{14}\text{H}_{22}\text{O}_3$. Calculated %: C 70.54; H 9.31.

Preparation of Decahydro-2-naphthaldehyde. The glycidic ester (70.6 g) was heated with a 20% potash solution (500 g) under mechanical stirring for 60 minutes. The solution obtained was cooled and carefully acidified with 18% hydrochloric acid; the glycidic acid, which separated as an oil, was then extracted with ether, and the ether extract was washed with water and dried over Na_2SO_4 . The solvent was driven off, and the residual gel-like mass was heated under reduced pressure, when the aldehyde formed distilled over; the fraction 80–130°/8 mm was collected. Refractionation yielded decahydro-2-naphthaldehyde (115–121°/13 mm) (about 26 g, 51.5%) and a semicarbazone, which crystallized from alcohol in rectangular plates, had m.p. 173–175°.

Found %: N 19.35; 19.40
 $\text{C}_{12}\text{H}_{21}\text{ON}_3$. Calculated %: N 18.83

Preparation of β -(2-Decalyl)- β -alanine (β -Aminodecahydro-2-naphthalenepropionic Acid). Decahydro-2-naphthaldehyde (8 g) was mixed at 0° with a 7% alcoholic solution of ammonia (12 ml, i.e. 10% excess), and malonic acid (5 g) was added to the white oily mass formed. The reaction mixture was heated on the water bath for five hours under reflux, and the crystalline mass obtained after removal of the alcohol was extracted with hot water. The insoluble residue was dried and washed with boiling benzene. The total yield of amino acid of m.p. 203–205° was 5.2 g, i.e. about 48% calculated on the amount of decahydronaphthaldehyde taken. Recrystallization from alcohol gave needles, m.p. 211°.

Found %: C 69.22; 69.30; H 10.39; 10.52; N 6.59; 6.43
 $\text{C}_{13}\text{H}_{23}\text{O}_2\text{N}$. Calculated %: C 69.27 H 10.29 N 6.22

Unsaturated acids present were extracted from the benzene solution by means of a 5% sodium carbonate solution. From the total amount (105 g) of decahydro-2-naphthaldehyde taken for all the preparations carried out, a yield of 14.5 g of unsaturated acids was obtained. The product as first obtained was an oil, which by fractional distillation under reduced pressure yielded a thick straw-yellow liquid over the range 210–215° at 23 mm. The acid was further purified through the sodium salt. The oil that separated on acidification gradually solidified and, after recrystallization from petroleum ether, it melted at 72–92°. The wide melting range is to be explained by the presence of a mixture of isomers. Values of 212.9 and 214 were found for the equivalent weight; the value calculated for $\text{C}_{13}\text{H}_{20}\text{O}_2$ is 208.16. The mixture of unsaturated acids was found to decolorize bromine water and permanganate solution. It was not studied further.

Preparation of the Benzoyl Derivative. To a solution prepared by dissolving β -(2-decalyl)- β -alanine (15 g) in a 10% caustic potash solution (110 g), benzoyl chloride (7.9 ml) was added at 2° over 15 minutes.

The reaction mixture was stirred for four hours, the temperature being gradually raised to 40° (the temperature was at about 40° for the last two hours). The solution was cooled and washed with ether, and the aqueous layer was acidified with hydrochloric acid (to Congo Red). The slowly crystallizing oil that separated was carefully washed with boiling water and cooled. The product was N-benzoyl-β-(2-decalyl)-β-alanine (18.8 g, 85.7 %), m.p. 140-143°.

Found %: N 4.25; 4.10

$C_{20}H_{27}O_3N$. Calculated %: N 4.25

The substance obtained was a mixture of isomers, for after it had been recrystallized three times from benzene, its melting point rose to 204-206° and did not change further. Analysis for nitrogen showed that the substance purified in this way was also N-benzoyl-β-(2-decalyl)-β-alanine ($C_{20}H_{27}O_3N$), i.e., this treatment had yielded one of the stereoisomeric forms in the pure state.

Found %: N 4.68; 4.59

$C_{20}H_{27}O_3N$. Calculated %: N 4.25

Preparation of the Isomeric Amides of N-Benzoyl-β-(2-decalyl)-β-alanine. The mixture of the cis and trans isomers of the benzoyl derivative of the amino acid having m.p. 140-143° (18.3 g) was heated with thionyl chloride (19.9 g) for 3 hours 30 minutes at 40-42°. The excess of thionyl chloride was driven off under reduced pressure, and the hard glassy mass of acid chlorides obtained was treated with dry ether. At first complete dissolution occurred, and then, from the solution obtained, a white crystalline precipitate came down. It was filtered off and washed with dry ether. This precipitate and the ether solution were each treated with dry ammonia under cooling. The ether-insoluble acid chloride yielded an amide of m.p. 200-205° (2.63 g), and after it had been recrystallized twice from alcohol, its melting point rose to 210-212° and did not change further.

Found %: C 73.29; 73.38; H 8.75; 8.82; N 8.55; 8.63

$C_{22}H_{29}O_2N_2$. Calculated %: C 73.12; H 8.60; N 8.53

Action of ammonia on the ether-soluble acid chloride yielded an amide of m.p. 180-205° (12.82 g). After two recrystallizations the melting point rose to 250-252°.

Found %: C 73.23; 73.03; H 8.69; 8.76; N 8.86; 8.81

In a mixed test on the two amides the melting point fell to 199°.

The total yield of pure recrystallized amides was about 40%.

Hydrolysis of the Amide of m.p. 210-212°. The amide (0.1 g) was heated for 5-6 hours with 12% hydrochloric acid (10 ml). Cooling of the solution yielded the benzamido acid (0.08 g), completely soluble in alkalis. After it had been recrystallized three times from alcohol, it melted at 186-188°. Analysis for nitrogen confirmed its structure.

Found %: N 4.62; 4.67

$C_{20}H_{27}O_3N$. Calculated %: N 4.25

In a similar manner (by means of concentrated hydrochloric acid) the amide of m.p. 250-252° was hydrolyzed. The benzamido acid obtained was recrystallized three times from benzene, but did not melt sharply (170-175°).

This product was evidently a contaminated preparation of the benzamido acid isomer referred to above.

Found %: N 4.36; 4.50

A mixed test on the two preparations gave a depressed melting point of 155°.

Action of Acetic Anhydride on the Amide of m.p. 210-212°. A mixture of the amide (0.62 g) and acetic anhydride (4.3 ml) was boiled gently for 10-12 hours. The solution obtained was cooled and filtered from the small amount of unchanged amide (0.02 g), and the excess of acetic anhydride was removed from the filtrate by heating it under reduced pressure. The residue was boiled with water, cooled, and extracted with ether. The ether extract was washed with a weak solution of alkali and then with water; it was dried over Na_2SO_4 . The ether was removed yielding a substance (0.36 g) of m.p. 116-129°. The melting point, after three recrystallizations from ether, was 158-159.5°. The analysis and properties of the substance obtained indicated it to be a (2-decalyl)-dihydromethyl-1(3H)-pyrimidone, formed as a result of a transacylation reaction.

Found %: N 11.05; 10.99
 $C_{15}H_{24}ON_2$. Calculated %: N 11.29

This reaction was confirmed also by an examination of the aqueous layer from which benzoic acid was isolated (0.23 g, almost theoretical yield).

Preparation of N-Carbamoyl- β -(2-decalyl)- β -alanine (Decahydro- β -ureido-2-naphthalenepropionic Acid). Sodium cyanate (0.35 g) was added to a boiling solution of β -(2-decalyl)- β -alanine (1 g) in water (16 ml), and heating was continued on a boiling water bath for 3-4 hours. When the solution was cooled and acidified, a rapidly crystallizing oil came down (1 g, about 84 %). The ureido acid, after recrystallization from alcohol (rectangular plates), melted at 205-206°.

Found %: N 10.59; 10.63
 $C_{14}H_{24}O_3N_2$. Calculated %: N 10.45

Preparation of 6-(2-Decalyl)-hydrouracil. The ureido acid (0.06 g) was heated with hydrochloric acid (15 ml, sp. gr. 1.17) for three hours over a gauze. At first there was complete solution, and then a crystalline precipitate formed, granular at first, turning gradually into leaflets. Concentration and cooling gave crystals of the hydrouracil compound (about 0.05 g, about 85%). After recrystallization from alcohol, the decalyl-hydrouracil melted sharply at 269-270°.

Found %: N 11.51; 11.54
 $C_{14}H_{22}O_2N_2$. Calculated %: N 11.20

Preparation of the Ethyl Ester of N-Benzoyl- β -(2-decalyl)- β -alanine. 1) Hydrogen chloride was passed for 5-6 hours at 60-75° into a solution of the benzoylated amino acid (2.4 g) in absolute alcohol (30 ml); the reaction mixture was then cooled to 0°, hydrogen chloride was passed to saturation, and the mixture was set aside overnight. The solvent was vacuum-distilled off, and the residue was washed with water and extracted with ether. The ether extract was washed with a weak solution of sodium bicarbonate and with water, and was dried over anhydrous sodium sulfate. After removal of ether, a rapidly crystallizing oil (2.6 g, m.p. 72-83°) remained; it melted after recrystallization from petroleum ether at 77-82° (2.46, about 94 %).

Found %: N 4.38; 4.25
 $C_{22}H_{31}O_3N$. Calculated %: N 3.92

2) An identical product was obtained by benzoylation of the ethyl ester of β -(2-decalyl)- β -alanine, the latter, which was prepared in the usual way, being dissolved in five times its weight of pyridine and treated with a small excess of benzoyl chloride at -5°. After prolonged standing at room temperature, the reaction mixture was washed with water and hydrochloric acid and extracted with ether. The ether extract was neutralized with a solution of sodium bicarbonate, washed with water, and dried over sodium sulfate. The rather thick oil that remained after removal of the solvent rapidly solidified; it melted after recrystallization from petroleum ether at 79-83° and did not depress the melting point of the ester prepared by the first method.

Preparation of the Hydrazide of N-Benzoyl- β -(2-decalyl)- β -alanine. The ethyl ester of N-benzoyl- β -(2-decalyl)- β -alanine (5.3 g) was added gradually (in four portions) to heated hydrazine hydrate (2.25 ml); some absolute alcohol (6 ml) was added to the last portion of the ester. The solution obtained was boiled gently for 60-75 minutes; an almost solid crystalline mass formed, and some absolute alcohol (5-6 ml) was therefore added and heating was continued for a further 30-40 minutes on a boiling water bath. The mixture was cooled, and the precipitate was filtered off and washed on the filter successively with water, alcohol, and ether. The hydrazide obtained (4.54 g, 89%) melted at 182-196°; after three recrystallizations from alcohol the melting point rose to 201.5-204.5°.

Found %: N 12.13; 12.31
 $C_{20}H_{29}O_2N_2$. Calculated %: N 12.24

Preparation of N-Benzoyl- β -(2-decalyl)- β -alanine Azide and of 3-Benzoyl-4-(2-decalyl)-2-imidazolidinone. The hydrazide of N-benzoyl- β -(2-decalyl)- β -alanine (1.75 g, m.p. 182-196°) was dissolved in 73-75% acetic acid (35 ml) and cooled to 0°. To this solution finely ground sodium nitrite (1.26 g) was added in 3-4 portions over a period of 15 minutes with shaking. The solution was allowed to stand for two hours at 0°, and

ice water was then added; the precipitate of azide that formed was filtered off and washed with ice water on the filter until the odor of acetic acid disappeared. The preparation was well pressed between filter papers and was mixed without drying with 95 ml of absolute benzene and then heated. The whole of the water present distilled over with 50 ml of benzene; the condenser was then reset in the reflux position, a further 45-50 ml of benzene was added to the reaction mixture, and boiling was continued for a further four hours. The solution was filtered hot to remove mechanical contamination, and the filtrate was concentrated, about 50 ml of benzene being driven off. The solution, on being cooled, yielded white needles of m.p. 210-217° (0.7 g). After evaporation of the mother liquor to dryness and washing of the residue with a small amount of ether, a further 0.59 g of material of m.p. 167-173° was obtained.

Both compounds, according to their properties and elementary analyses, appeared to be 3-benzoyl-4-(2-decalyl)-2-imidazolidinones. Thus, by means of the Curtius reaction it was found possible to bring about separation of the two stereoisomeric forms. The first product after recrystallization from benzene melted at 213-215°.

Found %: N 8.68; 8.53

The second was recrystallized from alcohol and then melted at 174-175°.

Found %: N 8.34; 8.28

$C_{20}H_{26}O_2N_2$. Calculated %: N 8.59

A mixed melting-point test on the two benzoyldecalylimidazolidinones showed a small but definite depression. The total yield of benzoyldecalylimidazolidinones was 1.29 g (about 78% of the hydrazide).

Preparation of 4-(2-Decalyl)-2-imidazolidinone. Nonpurified benzoyldecalylimidazolidinone of m.p. 210-217° was taken for hydrolysis; it was heated with 20% caustic soda on a water bath for 4-5 hours. Hydrolysis did not go very readily, and a greatly contaminated imidazolidinone compound was obtained having an extended melting range. After repeated recrystallization from alcohol, 4-(2-decalyl)-2-imidazolidinone, m.p. 254.5-258.5°, was obtained.

Found %: C 70.61; 70.37; H 10.23; 10.09; N 12.85; 12.73

$C_{13}H_{21}ON_2$. Calculated %: C 70.21; H 9.98; N 12.61

At the same time benzoic acid (about 64%) was isolated. Part of the benzoyl derivative remained unchanged even after a more prolonged heating with caustic soda.

SUMMARY

1. It has been established that by the decarboxylation of the glycidic acid $C_{10}H_{16}C(CH_2O)CH \cdot COOH$, obtained by Darzens' method from cis-decahydro-2-naphthol of m.p. 105°, a mixture of stereoisomeric decahydro-2-naphthaldehydes is formed; these have not been investigated further.
2. The synthesis has been effected, by Rodionov's method, of β -(2-decalyl)- β -alanine (β -amino-decahydro-2-naphthalenepropionic acid), which also appeared to be a mixture of isomers, the separation of which was not carried out.
3. By taking advantage of the different ether-solubilities of the acid chlorides of the N-benzoylated β -(2-decalyl)- β -alanines, the corresponding amides, m.p. 210-212° and 250-252°, were isolated.
4. The two amides were converted by careful hydrolysis into the isomeric N-benzoylated β -(2-decalyl)- β -alanines.
5. It has been shown that when the amide of N-benzoyl- β -(2-decalyl)- β -alanine is heated with acetic anhydride, a transacylation reaction occurs, and instead of 6-(2-decalyl)-5,6-dihydro-2-phenyl-4(3H)-pyrimidinone the corresponding 2-methyl derivative is obtained.
6. In order to characterize β -(2-decalyl)- β -alanine, the corresponding ureido acid and 6-(2-decalyl)-hydouracil were prepared.
7. Esters and hydrazides of N-benzoyl- β -(2-decalyl)- β -alanine have been prepared, and, by means of the Curtius reaction, they have been converted into 3-benzoyl-4-(2-decalyl)-2-imidazolidinones and the corresponding 4-(2-decalyl)-2-imidazolidinone.

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CONVERSION OF PENTANE INTO LIQUID HYDROCARBONS AND GAS AT 250-360 ATMOSPHERES AND 400-500°

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It was shown in one of our investigations [1] that pentane may be converted catalytically into liquid hydrocarbons and gas at 20-80°. This reaction can be brought about in a similar way also for propane and butane. The present investigation is concerned with the conversion of pentane into liquid and gaseous hydrocarbons at comparatively high temperatures.

The reactions undergone by pentane may proceed in several directions.

1. Cracking of pentane. The thermal reactions of pentane resulting from cracking at 400-500° and at atmospheric pressure lead to the formation of gaseous products only [2]. The gas formed in four hours at 396° contains 2 % of hydrogen, 19% of methane, 24% of ethane, 22% of propene, 9% of butenes, 2% of butane, and 12% of pentane; it contains also an insignificant amount of ethylene and propane. The product obtained by cracking isopentane at 550° is of similar composition. In cracking, therefore, the main process is the splitting of the pentane molecule with formation of methane, ethane, and other gaseous hydrocarbons, but no liquid products.

2. Destructive alkylation. It was shown by Paushkin and Fleish [1] that isopentane on long contact (several months) at 15-20° with aluminum chloride as catalyst is converted into gas and liquid hydrocarbons in the C₆-C₉ range. This process can be effected also in the course of an hour at 80° and 8-10 atm. in presence of 8-10% of aluminum chloride. The liquid distillate formed in this reaction distills over in the range 35-130° and corresponds in amount to 30-45% of the original isopentane. The gas formed corresponds in amount to 35-55% of the isopentane and contains about 60% by volume of isobutane. The liquid reaction products have an unsaturated character; the hexane fraction contains 2,2-dimethylbutane and 2-methylpentane.

This reaction may be regarded as a combined process in the first stage of which splitting (cracking) of isopentane into alkenes and alkanes occurs; in the second stage the alkenes formed alkylate the original isopentane molecule. In the first stage energy is used, and in the second, energy is given up. As a result of the combined cracking and alkylation reactions the expenditure of energy necessary in the first stage is compensated, and the process becomes possible at low temperatures.

As already mentioned, the destructive alkylation of the gaseous hydrocarbons, propane and butane, can be brought about in a similar way to that of pentane. Results have been recently published on the destructive alkylation of propane, butane, and pentane in presence of PF₃ + HF as catalyst [3]. This catalyst acts similarly to aluminum chloride. The reaction with propane was carried out in an autoclave (47 atm, 85°, 2 hr.). The extent of conversion of the propane was 10%. The reaction products contained 5.7% of ethane, 82.8% of isobutane, and 11.5% of hydrocarbons bound by the catalyst.

The reaction was carried out with butane at 50° for 0.5-2 hours under a pressure of about 24 atm. over the same catalyst. Conversion of butane into liquid hydrocarbons attained 8.5%; about 50% of the original butane isomerized into isobutane. The destructive alkylation of pentane over EF₃ + HF proceeded with a conversion of 24%. The reaction was carried out at 85° under a pressure of 21 atm., but it was found that, in presence of 2% of pentene, the reaction temperature could be lowered to 32° for a period of contact with a catalyst of 30 minutes. Under these conditions 23-24% of the pentane was converted into high-boiling hydrocarbons.

3. Isomerization of pentane. Moldavsky and coworkers [4], in a study of the isomerization of pentane in presence of aluminum chloride, noted that, in addition to the main reaction product, isopentane, hexanes, mainly 2,2-dimethylbutane, were formed as by-products. The formation principally of 2,2-dimethylbutane was explained by the authors of this paper by the greater ease of methylation of the hydrogen of a tertiary carbon atom, as compared with that of hydrogens in other groups.

However, this hypothesis is doubtful, for it is difficult to explain from this point of view the fact, observed by them, of the formation of isopentane instead of the expected 2,2-dimethylpropane in the isomerization of butane in presence of aluminum chloride. The simultaneous formation of high-boiling hydrocarbons

in the isomerization of pentane is pointed out also in other published papers [5]. Thus, isomerization of pentane is accompanied by destructive alkylation, leading to the formation of hydrocarbons boiling higher than the original pentane.

4. Formation and further reaction of pentane during thermal alkylation. Pentane and isopentane are formed during the thermal alkylation of propane by ethylene at 500° and 300 atm. [6]. The liquid reaction products consist of pentane and isopentane (73%) and a C_6-C_9 fraction (27%) containing about 15-20% alkenes. The gas formed in the thermal alkylation of propane with ethylene consists approximately of 50% methane, 20% ethane, and 30% butane (without considering unchanged propane and ethylene). Thus, in addition to the main reaction, alkylation of propane by ethylene to pentanes, destructive alkylation occurs, yielding hexanes, octanes, and nonanes. The gas formed is essentially methane.

EXPERIMENTAL

The experiments on the thermal conversion of pentane were carried out in a rotating autoclave, 500 ml in capacity. In this a pentane fraction (about 300 ml) was placed; it boiled in the range 32-38° and had d_4^{20} 0.6238; n_D^{20} 1.3575, and a bromine number of zero. The distillation curve of the initial fraction is shown in Figure 1. Thus, the pentane fraction used as raw material consisted essentially of n-pentane, and in future it will be referred to as pentane. The autoclave was heated by means of an electric furnace, and the temperature in the autoclave was measured and controlled within the set range by the aid of an alumel-chromel thermocouple connected to a PM-47 electronic galvanometer. At the end of the experiment the autoclave was cooled to room temperature and the gaseous reaction products were passed out of the autoclave through a system of traps, cooled by a cooling mixture to below 0°, in order to hold back pentane. The gas then passed through a gas meter, after which part of the gas proceeded to a gasholder for analysis and the remainder passed out into the atmosphere. The liquid reaction products in the autoclave consisted of a mixture of unchanged pentane and the higher-boiling liquid hydrocarbons formed. The unchanged pentane was distilled off through a fractionating column within the boiling limits of the original material, and the remaining, heavier hydrocarbons were fractionated through a column of 35 theoretical plates and investigated further as described below. The composition of the gas obtained in a number of pentane-conversion experiments was determined by fractionation through a low-temperature fractionation column.

Thermal Conversion of Pentane

The thermal conversion of pentane was carried out in absence of catalysts in the temperature range 350-450°. The effect of temperature on the progress of pentane conversion was investigated for constant duration of reaction (two hours). The results obtained are given in Table 1 and Fig. 2.

At 350° pentane did not undergo conversion, appreciable reaction commencing only at temperatures above 375°. It follows from the results given in Table 1 that the optimum temperature for the conversion of pentane into higher-boiling liquid hydrocarbons is in the range 450-460°, the corresponding pressure being 250-310 atm. At 480° and above, splitting of pentane with formation of a large amount of gaseous hydrocarbons takes place.

A further series of experiments was carried out with the aim of determining the effect of the duration of the reaction on the degree of conversion of the pentane. The results of this series of experiments are shown in Table 2 and are presented graphically in Figure 3.

As will be seen from the results cited, a sufficient degree of conversion into liquid products is attained in two hours; increase in the time to three hours increases the amount of gaseous products.

As a result of a number of successive experiments under optimum conditions (2 hrs., 450-455°, 300-350 atm) 450 g of liquid products boiling higher than the original pentane was accumulated. These products were fractionated and investigated as described below. The liquid product extracted from the autoclave had the following characteristics: d_4^{20} 0.6776; n_D^{20} 1.4046.

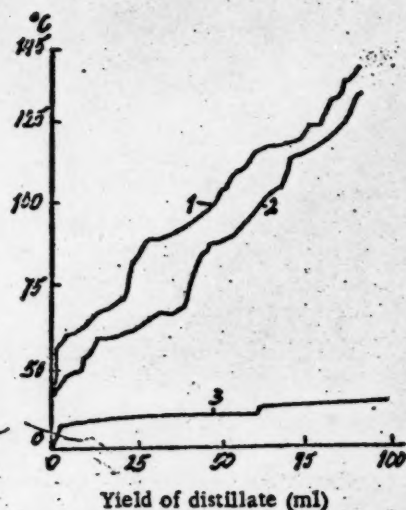


Fig. 1. Distillation curves for the conversion products of the pentane fraction and for the raw material: 1) thermal process; 2) aluminosilicate catalyst; 3) original raw material.

TABLE 1

Effect of Temperature on the Yield of Products of the Thermal Conversion of Pentane

Temp. of expt. (mean) (°C)	Pressure (mean) (atm)	Amt. of unchanged pentane (%)	Amt. of conversion products (%)	
			liquid	gaseous
350	200	100.0	0	0
375	218	93.9	6.0	—
415	230	81.2	14.1	4.7
453	260	66.5	22.1	11.4
460	310	64.2	23.2	12.6
480	510	39.3	16.2	44.5

TABLE 2

Effect of Time on the Degree of Conversion of Pentane

Reaction time (hr.)	Temperature (°C)	Pressure (mean) (atm.)	Amt. of unchanged pentane (%)	Amt. of reaction products (%)	
				liquid	gaseous
0.25	450	210	99.0	1.0	—
1.0	450	310	81.3	12.4	6.3
2.0	460	325	64.8	23.2	12.0
3.0	455	310	73.0	12.2	14.5

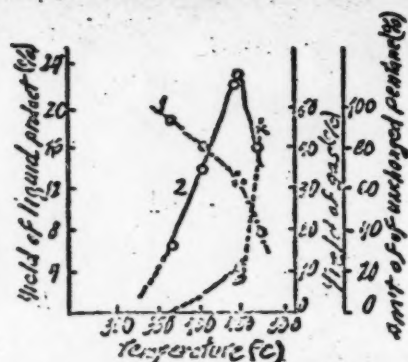


Fig. 2. Effect of temperature on the yield of products of the thermal conversion of the pentane fraction: 1) pentane; 2) liquid product; 3) gaseous product.

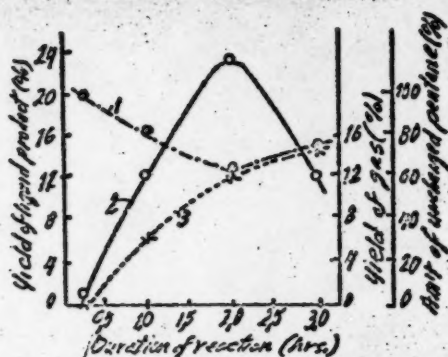


Fig. 3. Effect of time on the yield of products of the thermal conversion of the pentane fraction: 1) pentane; 2) liquid product; 3) gaseous product.

The product was fractionated through a column of 25 theoretical plates and consisted of 63% (by volume) of a fraction boiling up to 150°, called the gasoline fraction, and 37% of a fraction boiling above 150° and up to 300°. The specific gravity of the mixture of hydrocarbons boiling above 40° was $d_4^{20} = 0.7469$; n_D^{20} was 1.4238, the bromine number was 18.2, and the content of sulfonatables, determined by means of Kattwinkel's mixture, was 28 %.

The gasoline fraction had the following constants: $d_4^{20} 0.7201$; $n_D^{20} 1.4087$; bromine number 24.5; content of sulfonatables, determined by means of Kattwinkel's mixture, 8.3%. The octane number of this fraction, determined by the engine method, was 67 points.

Narrow fractions, separated by fractionation of the gasoline fraction through a column of 35 theoretical plates, were subjected to qualitative spectrum analysis, the Raman spectra being employed.*

The results of the analysis of the fractions obtained are given in Table 3.

Apart from the hydrocarbons indicated, an insignificant amount of unsaturated hydrocarbons was detected in all fractions. Thus, in the thermal conversion of pentane a variety of hydrocarbons is obtained, the formation of which is associated, evidently, with the reactions of destructive alkylation, cyclization, and cracking of pentane followed by polymerization of unsaturated hydrocarbons.

The gas formed in the thermal conversion of pentane was fractionated in a low-temperature fractionation apparatus in order to determine its composition. The results of the analysis are given in Table 4.

* The spectrum analysis was carried out by M. V. Shishkina, and we take this opportunity of thanking her.

TABLE 3

Hydrocarbons Detected among the Products of the Thermal Conversion of Pentane*

Boiling range of fraction (°C)	Refractive index n_D^{20}	Hydrocarbons detected
56-65	1.3810	2-Methylpentane, 3-methylpentane, 2,3-dimethylbutane
65-70	1.3891	Hexane, 2-methylpentane
80-90	1.3961	Benzene, 3-methylhexane, 2-methylhexane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, cyclohexane
90-95	1.3980	3-Methylhexane, 3-ethylpentane
95-105	1.458	Heptane, toluene, methylcyclohexane
110-118	1.4050	4-Methylheptane, 3-ethyl-2-methylpentane
118-125	1.4098	Octane, 4-methylheptane

* The principal hydrocarbons boiling within the limits indicated are given in Table 3. Hydrocarbons that occur in more than one fraction are indicated only for those fractions in which they are contained in considerable amount.

Conversion of Pentane in Presence of Catalysts

The conversion of pentane into liquid and gaseous hydrocarbons was studied in presence of a number of oxide catalysts—on aluminosilicate cracking catalyst, on aluminochrome and aluminomolybdenum catalysts, and on active aluminum oxide. The experimental procedure was similar to that used in the thermal conversion of pentane. Experiments were of two-hours' duration, and the amount of pentane taken in all experiments was 155 g. In order to investigate the effect of temperature on the thermocatalytic conversion of pentane, a number of experiments were carried out in presence of aluminosilicate cracking catalyst over the range 350-480°. The results obtained are given in Table 5.

TABLE 5

The Effect of Temperature on the Conversion of Pentane in Presence of an Aluminosilicate Catalyst*

Temperature (°C)	Pressure (atm.)	Amt. of catalyst (%)	Amt. of unchanged pentane (%)	Amount of conversion products (%)	
				liquid	gaseous
350	180	10.0	100.0	—	—
400	200	10.0	82.9	16.5	0.6
450	275	11.0	72.0	22.7	5.0
480	~600	21.0	32.7	21.3	46

* A fresh portion of catalyst was taken for each experiment.

The results given in Table 5 are presented graphically in Fig. 4. As in the case of the purely thermal conversion of pentane, the optimum conversion temperature for the conversion of pentane into higher-boiling hydrocarbons is about 450°. Further experiments were carried out at 450-460° for two hours with different catalysts. The results of this series of experiments are given in Table 6. As will be seen from the results given, the aluminosilicate

TABLE 4

Composition of the Gas Formed in the Thermal Conversion of Pentane at 450° and 500 atm.

Component	Content (vol. - %)
H ₂	2.5
CH ₄	65.2
C ₂ H ₆	22.3
C ₂ H ₄	0.1
C ₃ H ₈	4.6
C ₃ H ₆	0.3
ΣC ₄ H ₁₀	1.4
Residue	3.6
	100.0

The density of the gas obtained in the various experiments was 0.79-0.81 g/liter. Thus, the gas consisted mainly of methane with very little admixture with unsaturated hydrocarbons. The gas obtained differed from the gases obtained in the thermal cracking of pentanes by being almost free from unsaturated hydrocarbons, but it was very near in composition to the gas formed by thermal alkylation of, for example, propane by means of ethylene (see above).

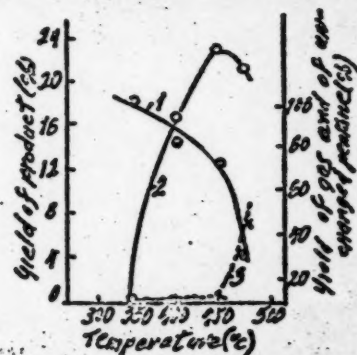


Fig. 4. Effect of temperature on the yield of conversion products of the pentane fraction at an aluminosilicate catalyst: 1) pentane, 2) liquid product, 3) gaseous product

TABLE 6

Effect of Various Catalysts on the Conversion of Pentane (450°, 280 atm.)

Catalyst	Conversion of pentane (%)	Yield of products (%)			Characteristics of gasoline fraction		
		gas	Fraction, b.p. 40-150°	Fraction, b.p. 150-300°	n_D^{20}	d_4^{20}	Bromine number
Aluminosilicate	36.9	15.9	12.4	8.62	1.3982	0.6923	19.8
Aluminosilicate (second sample)	30.8	12.8	12.1	5.9	1.3950	0.6908	19.5
Activated aluminum oxide	33.9	16.0	15.3	8.6	1.3990	0.7023	25.3
Aluminochrome	36.0	11.7	15.4	8.9	1.4060	0.7235	23.8
Aluminummolybdenum	34.6	14.1	12.9	7.65	1.4042	0.7081	25.5
Catalyst absent	35.2	12.0	13.5	9.7	1.4087	0.7201	24.6

catalyst did not alter the experimental conditions to a significant extent, but its presence resulted in a lowering of the specific gravity of the gasoline fraction (from 0.72 to 0.69) and a rise in the total yield of low-boiling hydrocarbons in the gasoline fraction.

Aromatization catalysts (aluminochrome and aluminummolybdenum) had no essential effect on the pentane conversion process. The distillation curves for the products of thermocatalytic conversion of pentane are given in Fig. 1. The gasoline obtained by the catalytic process, as is shown by the distillation results, is considerably lighter than the product of the purely thermal process.

TABLE 7

Composition of the Gas Obtained in the Conversion of Pentane at an Aluminosilicate Catalyst.

Component	Content (vol. -%)	
	Temp. of expt. 450°	Temp. of expt. 500°
H ₂	2.0	0.02
CH ₄	60.6	7.8
C ₂ H ₆	26.0	—
C ₃ H ₈	—	0.8
C ₃ H ₆	6.1	46.7
iso-C ₄ H ₈	—	0.3
C ₄ H ₈	—	1.0
iso-C ₄ H ₁₀	1.0	21.1
n-C ₄ H ₁₀	4.3	13.4
Residue	—	8.9
	100.0	100.0

The gas obtained in the catalytic conversion of pentane at an aluminosilicate catalyst had the composition shown in Table 7. As will be seen from these results, the gas formed at 450° consisted, as in the case of thermal conversion, mainly of methane, but the gas formed at 500° was much different in composition, the heavier hydrocarbons propane and isobutane being formed. This extremely interesting fact merits special study.

The narrow fractions of gasoline, obtained by fractionation, were qualitatively analyzed by the aid of Raman spectra. The results of the spectrum analysis are given in Table 8. Apart from the hydrocarbons indicated in this table, all the fractions contained unsaturated hydrocarbons, which was confirmed also by the value of the bromine number (19.5) for the gasoline obtained by the catalytic conversion of pentane.

From a comparison of the compositions of the gasoline of the thermal process and of that resulting from

TABLE 8

Hydrocarbons Detected in the Products of the Conversion of Pentane at an Aluminosilicate Catalyst

B.p. of fraction (°C)	n_D^{20}	Hydrocarbons detected
42-50	1.3875	Cyclopentane, pentane, 2,2-dimethylbutane
50-58	1.3860	Cyclopentane, 2,2- and 2,3-dimethylbutanes
58-61	1.3751	2-Methylpentane, 2,3-dimethylbutane
61-65	1.3770	2- and 3-Methylpentanes, 2,3-dimethylbutane
65-70	1.3841	Hexane, 3-methylpentane
70-85	1.3907	Methylcyclopentane, benzene, 2,2- and 2,4-dimethylpentanes, 2,3-dimethylpentane
85-91	1.3939	2- and 3-Methylhexanes, 2,3- and 3,3-dimethylpentanes
91-101	1.4005	Heptane, 3-ethylpentane, 3-methylhexane, trans-1,2-dimethylcyclopentane
101-110	1.4073	Toluene, 2,4-dimethylhexane
110-118	1.4051	2,4- and 3,4-Dimethylhexanes, toluene
118-125	1.4067	2- and 4-Methylheptanes, 1,2-dimethylcyclohexane
125-133	1.4240	Octane, m- and p-xylenes, ethylbenzene

catalytic conversion of pentane, it may be stated that the gasoline obtained in the catalytic process contains a greater amount of branched hydrocarbons; also, the catalyst encourages aromatization. The formation of cycloalkanes is also very interesting. The gasoline from the catalytic process has also a somewhat higher octane number (69.2).

Thus, the investigation of the thermal and catalytic conversion of pentane under the conditions of thermal alkylation (400-500° and 300 atm.), indicates the possibility of the conversion of pentane into gas and liquid hydrocarbons, the formation of which from pentane is associated with the coupling of the reactions of cracking and alkylation, i.e., destructive alkylation, and with the polymerization process that usually accompanies the thermal alkylation reaction. The gas from the thermal conversion of pentane (which contains about 60-65% of methane) is very close in composition to the gas from thermal alkylation (which contains 50-55% of methane). The content of unsaturated hydrocarbons in the liquid products is of the same order in each case (about 15%).

The results obtained suggest that the conversion of pentane at 400-500° and 300 atm. proceeds by the reaction of thermal destructive alkylation. An aluminosilicate catalyst causes an increased yield of light products and reduced formation of unsaturated compounds.

In conclusion, it is our pleasant duty to express our thanks to A. A. Bashilov for his great assistance in the preparation of the original pentane.

SUMMARY

1. The thermocatalytic conversion of pentane at 450-460° and about 300 atm. has been investigated.
2. It has been shown that pentane, in absence of catalysts, undergoes a number of reactions, forming gaseous and liquid hydrocarbons. The composition of the mixture of hydrocarbons formed gives evidence of the occurrence of the reactions of destructive alkylation, cyclization, cracking, and polymerization.
3. It has been established that the use of certain oxide catalysts does not lead to a lowering of the reaction temperature, but affects the composition of the mixture of hydrocarbons formed; this is distinguished by the presence of a larger amount of branched hydrocarbons, and also of cycloalkanes, including cyclopentane hydrocarbons.

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CATALYTIC REACTIONS OF FIVE- AND SIX-MEMBERED CYCLOALKANES UNDER A PRESSURE OF HYDROGEN AT HIGH TEMPERATURE

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The extensive study of the catalytic reactions of five- and six-membered cycloalkanes carried out by a number of investigators has resulted in the establishment of some important regularities that permit us to predict the nature of their reactions and the way in which they depend on the nature of the catalysts and reaction conditions. Thus, already in 1911 Zelinsky [1] showed that six-membered cycloalkanes are smoothly converted into the corresponding aromatic hydrocarbons at 300° in presence of platinum or palladium black.

In 1934, in a study of the aromatization of narrow fractions of Emben (Novo-bogatin) gasoline in presence of nickel-alumina catalyst, one of us, working in conjunction with Zelinsky [2], found that the catalysis products contained aromatic hydrocarbons in appreciably larger amount than that to be expected if only the dehydrogenation of six-membered cycloalkanes occurred. On the basis of these experimental results, the suggestion was then made for the first time, by these authors, that under the given conditions there occurred not only dehydrogenation of six-membered cycloalkanes, but also other reactions, which led to the formation of aromatic hydrocarbons from hydrocarbons of other classes.

In the same year, 1934, Zelinsky and Kazansky [3] showed that, under the conditions of dehydrogenation catalysis in presence of platinized charcoal, five-membered cycloalkanes react with opening of the ring and formation of alkanes. Later, Kazansky and Flate [4] found that, under the same conditions, in addition to hydrogenolysis of five-membered cycloalkanes, there occurred also the dehydrocyclization of the alkanes formed with formation of small amounts of aromatic hydrocarbons.

It must be noted that, in presence of platinized charcoal in ordinary pressure, these reactions proceed already at about 300-330°; further rise in temperature leads to appreciable destruction of the substances undergoing catalytic reaction with formation of gaseous hydrocarbons and carbonaceous deposits that rapidly deactivate the catalyst. Oxide catalysts bring about various reactions of the cycloalkanes only at temperatures above 400°. However, they then lose their activity fairly rapidly.

In this connection we considered it to be of interest to study the reactions of some individual five- and six-membered cycloalkanes in presence of a mixed oxide-metal catalyst under a high pressure of hydrogen and at a high temperature. It was considered that increase in hydrogen pressure would greatly increase the stability of the catalyst and that the simultaneous action of pressure and elevated temperature would permit deeper and more varied reactions to be effected with the original hydrocarbons.

EXPERIMENTAL

The experiments that we have carried out, in which we have studied the reactions of cyclopentane, methylcyclopentane, and cyclohexane under a pressure of 15-20 atm. of hydrogen at 460° in presence of platinized alumina, fully confirmed our suppositions. The experiments with these cycloalkanes were carried out in a specially constructed apparatus of the flow type, which permitted exact control of temperature, pressure, and rate of passage of the original hydrocarbons. The rate at which hydrogen was supplied to the reactor was measured by means of a rheometer calibrated for the pressures employed in the experiments. The temperature of the reaction zone was recorded by an autographic galvanometer. Analysis of catalyzates was carried out by separating aromatic hydrocarbons by chromatographic adsorption and subsequently fractionating both aromatic and cycloalkane-alkane parts of the catalyzate through a column having an efficiency of 70 theoretical plates. The original cycloalkanes were first distilled through the same fractionation column. Their properties are given in Table 1.

Cyclopentane

Cyclopentane (238.2 g, i.e., 320 ml) was brought into contact with the platinum-alumina catalyst at

TABLE 1
Properties of the Original Cycloalkanes

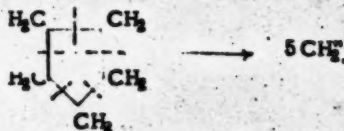
Cycloalkane	B.p. (°C at 752 mm)	n_D^{20}	d_4^{20}	MR _D	
				Calculated	Found
Cyclopentane	49.5	1.4070	0.7445	23.09	23.17
Methylcyclopentane	71.5	1.4115	0.7496	27.71	27.88
Cyclohexane	80.8	1.4268	0.7789	27.71	27.71

TABLE 2
Fractional Composition of the Cycloalkane-Alkane Part of the
Cyclopentane Catalyzate

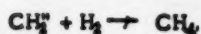
Frac- tion No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mix- ture of hydrocar- bons taken for frac- tionation	On orig- inal cyclo- pentane
1	27-29	12.0	7.4	1.3545	0.6201	14.2	10.0
2	29-38	35.5	22.2	1.3575	0.6267	42.7	34.5
3	38-52	25.5	19.0	1.4050	0.7453	36.5	22.8
4	52-73.5	3.0	2.2	1.4097	0.7480	4.2	3.0
	Residue	0.8	0.6	1.4097	—	1.1	0.5

to Ulmann's permanganate oxidation. From the mixture of crystalline carboxylic acids produced, the following were separated by the method of Moldavsky, Kamusher, and Kobyskaya [5]: benzoic acid (0.07 g; m.p. 121.6° after sublimation) and terephthalic acid (0.385 g), which was identified by conversion into its dimethyl ester (m.p. 140°).

It follows from the results cited that in the catalytic conversion of cyclopentane under the chosen conditions, the predominating reaction is the opening of the five-membered ring with formation of pentane (Fraction 2, Table 2). Simultaneously with this main reaction there occurs partial isomerization of pentane into 2-methylbutane (Fraction 1). However, special attention should be paid to the fact that appreciable amounts of methylcyclopentane (Fraction 4) and aromatic hydrocarbons, in particular benzene, toluene, and xylene, are found in the catalyzate. These new facts give convincing proof that, under the given conditions of catalytic action, cyclopentane undergoes a number of complex reactions, in which, in our opinion, an important part is played by methylene radicals, which arise as a result of the breakdown of the cyclopentane ring under the action of the platinized alumina catalyst:



A great proportion of these transient, very reactive radicals is rapidly hydrogenated to methane:



and others react with unchanged cyclopentane, causing methylation with formation of methylcyclopentane:

460° and 20 atm, at a space velocity of 0.43. The liquid catalyzate (184.3 g, i.e., 258 ml; 77.4% yield) had n_D^{20} 1.3960 and d_4^{20} 0.7315. It was notable that it contained 9% by volume of aromatic hydrocarbons. The aromatic hydrocarbons (17.1 g) isolated from the catalyzate had n_D^{20} 1.4980 and d_4^{20} 0.8705; the remaining, principal part (cycloalkane-alkane) had n_D^{20} 1.3850 and d_4^{20} 0.6754. In Table 2 and Fig. 1 results are given of the precise fractionation of 52.0 g of the cycloalkane-alkane part of the catalyzate.

In the fractionation of 17.1 g of aromatic hydrocarbons from the cyclopentane catalyzate at 749.5 mm, benzene having n_D^{20} 1.5005 (14.0 g, 81.9% of total amount of aromatic hydrocarbons) was isolated; the residue (2.9 g) distilled over in the range 85-215° and had n_D^{20} 1.5380. From this residue, by distillation over sodium, a fraction (0.9 g) boiling in the range 85-160° was separated, and this was subjected

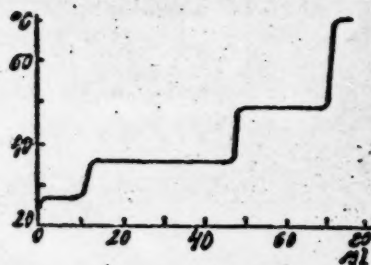
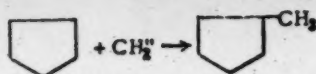
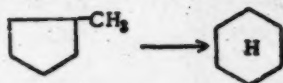


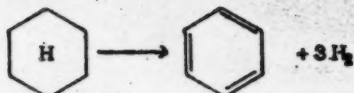
Fig. 1. Fractionation of the cycloalkane-alkane part of the cyclopentane catalyzate.



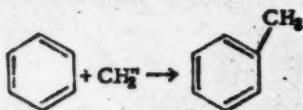
The greater part of the latter, under the given conditions, undergoes ring enlargement with formation of cyclohexane:



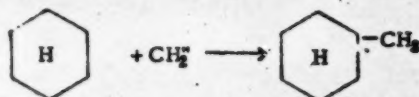
which is practically completely dehydrogenated to benzene:



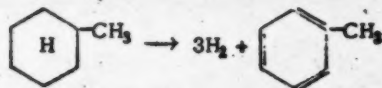
Part of the benzene formed is alkylated under the influence of the platinum-alumina catalyst (reacting similarly to cyclopentane), toluene being formed:



Further reaction gives xylene. The formation of toluene, however, may, with less probability, be represented also as the result of the alkylation of cyclohexane by methylene radicals, giving methylcyclohexane:

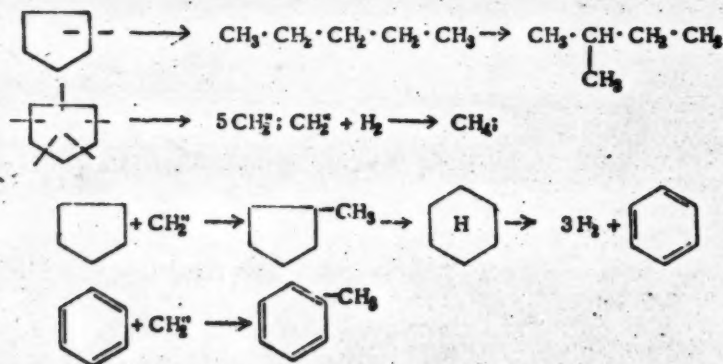


and subsequent catalytic dehydrogenation with formation of toluene:



The aromatic hydrocarbons accompanying toluene and xylene in the fraction having an upper distillation limit of 215° probably consist of a complex mixture of the products of the further methylation of benzene (polymethylbenzenes), but, owing to lack of material, this mixture of aromatic hydrocarbons was not investigated.

Thus, the complex catalytic reactions of cyclopentane under the chosen conditions may most probably be represented in the following scheme:



Analogous decomposition of cyclohexane, occurring at a nickel-alumina catalyst at 350-375° and giving methylene radicals, which alkylate benzene with formation of toluene and xylene, has already been observed by one of us and Zelinsky [6].

Methylcyclopentane

In the reaction, methylcyclopentane (374.8 g, i.e., 500 ml) was passed over the same catalyst at 460° under a pressure of hydrogen of 15 atm. and at a space velocity of 0.43. The resulting catalyzate (343.6 g, i.e., 453 ml; 91.7%) had n_D^{20} 1.4250 and d_4^{20} 0.7586; it contained 32.0% by volume of aromatic hydrocarbons. The aromatic part was separated, for investigation, from the cycloalkane and alkane parts by the chromatographic method. In Table 3 and Fig. 2 results of the analytical fractionation of the cycloalkane-alkane part of the catalyzate are given.

The cycloalkane-alkane part of the catalyzate taken for investigation (72.4 g) had n_D^{20} 1.3870 and d_4^{20} 0.7238 (Table 3). The aromatic hydrocarbons (72.1 g) separated from the methylcyclopentane catalyzate had n_D^{20} 1.4980 and d_4^{20} 0.8761. Results on the fractionation of these hydrocarbons are given in Table 4.

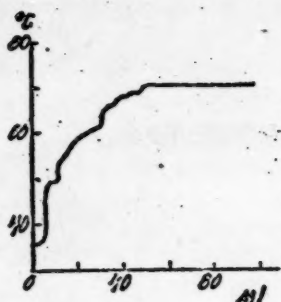


Fig. 2. Distillation curve for the cycloalkane-alkane part of the methylcyclopentane catalyzate.

As will be seen from the experimental results and from Table 4, a notable place among the products of the catalytic conversion of methylcyclopentane is occupied by aromatic hydrocarbons, among which, in addition to the predominating benzene, toluene, xylenes, and higher benzene homologs occur in small amounts.

On the basis of the results of the fractionation of the cycloalkane-alkane and aromatic parts of the methylcyclopentane catalyzate and of a comparison of the properties of the isolated fractions with the constants of individual hydrocarbons, it may be seen that in the catalytic conversion of methylcyclopentane enlargement of the five-membered ring to a six-membered ring occurs, and the latter is then completely dehydrogenated to benzene. Also, as a result of the hydrogenolysis of the methyl group of methylcyclopentane, cyclopentane is formed in appreciable amount:

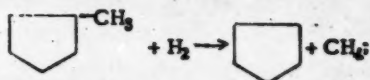
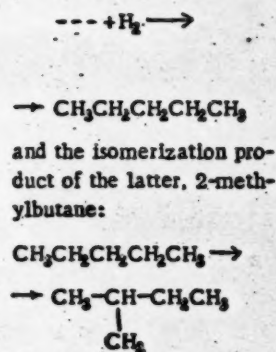


TABLE 3

Fractional Composition of the Cycloalkane-Alkane Part of the Methylcyclopentane Catalyzate.

Fraction No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocarbons taken for fractionation	On original methylcyclopentane
1	26-29	2.0	1.2	1.3540	0.6205	1.7	1.3
2	29-36	5.0	3.1	1.3580	0.6280	4.3	3.1
3	48-55.6	10.0	7.3	1.3910	0.7327	10.1	6.2
4	55.6-62.5	15.1	10.2	1.3765	0.6735	14.1	9.4
5	62.5-69	14.0	9.5	1.3765	0.6780	13.1	8.8
6	69.0-71.5	43.0	32.2	1.4115	0.7482	44.5	27.0
	Residue	10.0	7.5	1.4115	0.7480	10.4	6.2

also its hydrogenolysis product, pentane:



Simultaneously with these reactions hydrogenolysis of the methylcyclopentane ring occurs with formation of hexane and its isomers (see Fractions 5 and 4, Table 3).

Thus, methylcyclopentane, like cyclopentane, undergoes various reactions under the chosen conditions, giving a complex mixture of aromatic, cycloalkane, and alkane hydrocarbons in accordance with the following scheme:

TABLE 4

Fractional Composition of the Aromatic Part of the Methylcyclopentane Catalyzate

Frac- tion No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocar- bons taken for fraction- ation	On origi- nal methyl- cyclo- pentane
1	to 79.5	0.5	0.4	1.4980	—	0.6	0.2
2	79.5-80.1	70.0	61.3	1.5015	0.8765	85.0	25.7
3	80.1-109.5	0.2	0.18	1.4970	—	0.2	0.1
4	109.5-110.5	2.5	2.2	1.4960	0.8670	3.0	0.9
5	126-148	2.6	2.3	1.4970	0.8650	3.2	0.9
	Residue	4.2	3.7	1.5590	—	5.1	1.5

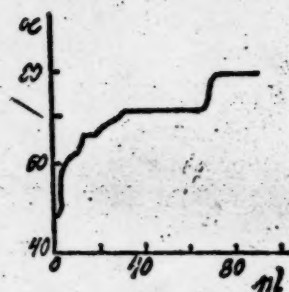
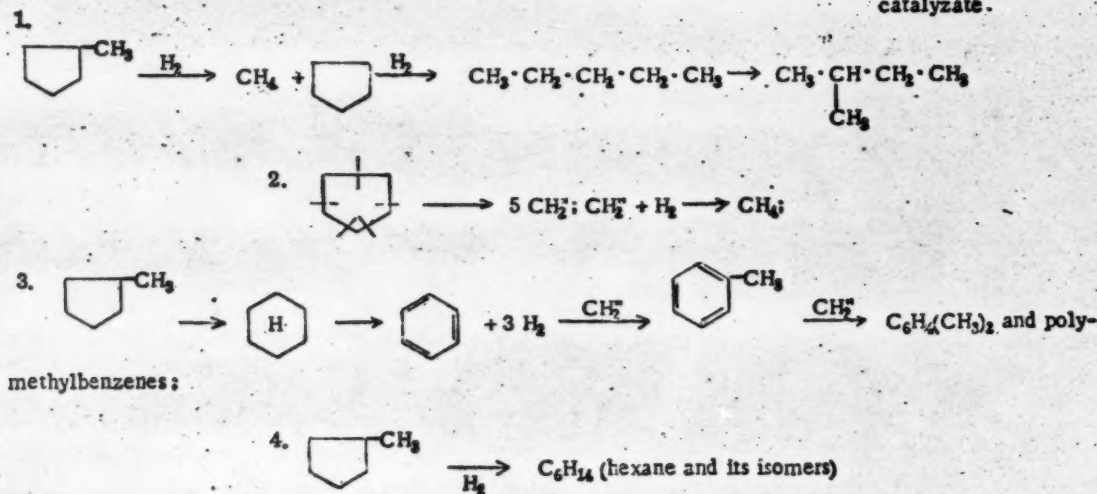


Fig. 3. Distillation curve for the cycloalkane-alkane part of the cyclohexane catalyzate.



In this case also, toluene, xylenes, and also polymethylbenzenes result from the methylation of benzene by methylene radicals formed by the "methane breakdown" of cyclopentane and also, possibly, of cyclohexane [6].

Cyclohexane

In the reaction, cyclohexane (934.7 g, i.e. 1200 ml) was treated at 460° and 15 atm. pressure of hydrogen. The catalyzate obtained (1060 ml, i.e. 873.1 g; yield 93.4%) had the following properties: n_D^{20} 1.4825, d_4^{20} 0.8237, 85% content by volume of aromatic hydrocarbons. The cycloalkane-alkane part of the catalyzate taken for investigation (107 ml, i.e. 75.9 g) had n_D^{20} 1.4165 and d_4^{20} 0.7097. The results of analytical fractionation through a column of 70 theoretical plates are given in Table 5 and Fig. 2.

The aromatic hydrocarbons, separated by the chromatographic method, had n_D^{20} 1.4980 and d_4^{20} 0.8745. A part of the mixture was fractionated into narrow fractions. The results of the analytical fractionation of 60 ml (52.6 g) of aromatic hydrocarbons are given in Table 6.

As will be seen from the results given in Tables 5 and 6, the main part of the cyclohexane catalyzate, obtained under high pressure and temperature conditions, consists of aromatic hydrocarbons, comprising about 87% of benzene and small amounts of toluene, xylenes, and polyalkylbenzenes. Oxidation of Fraction 3 (110-110.5°) by permanganate, according to Ullmann, gave benzoic acid, m.p. 121.2°; and from the products of the oxidation of Fraction 4 (110.5-148°) by the same method, benzoic acid (m.p. 121°) and a mixture of benzene-dicarboxylic acids (m.p. 287°) were isolated. The cycloalkane-alkane part of the catalyzate from cyclohexane contains a considerable amount (about 45%) of methylcyclopentane (Fraction 4, Table 5), some alkanes of

normal and branched structure (Fraction 3, Table 5), and a comparatively small amount of unchanged cyclohexane (9.2%).

TABLE 5
Fractional Composition of the Cycloalkane-Alkane Part of the Cyclohexane Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocarbons taken for fractionation	On original cyclohexane
1	28-38	4.0	2.5	1.3570	0.6258	3.3	0.5
2	38-66	20.0	13.1	1.3795	0.6537	17.3	2.6
3	66-69.5	11.0	7.3	1.3986	0.6682	9.6	1.4
4	69.5-72.0	45.0	33.7	1.4095	0.7483	44.4	6.0
5	72.0-78.9	15.0	11.3	1.4175	0.7518	14.9	2.3
	Residue (78.9-80.5)	9.0	7.0	1.4268	0.7785	9.2	1.2

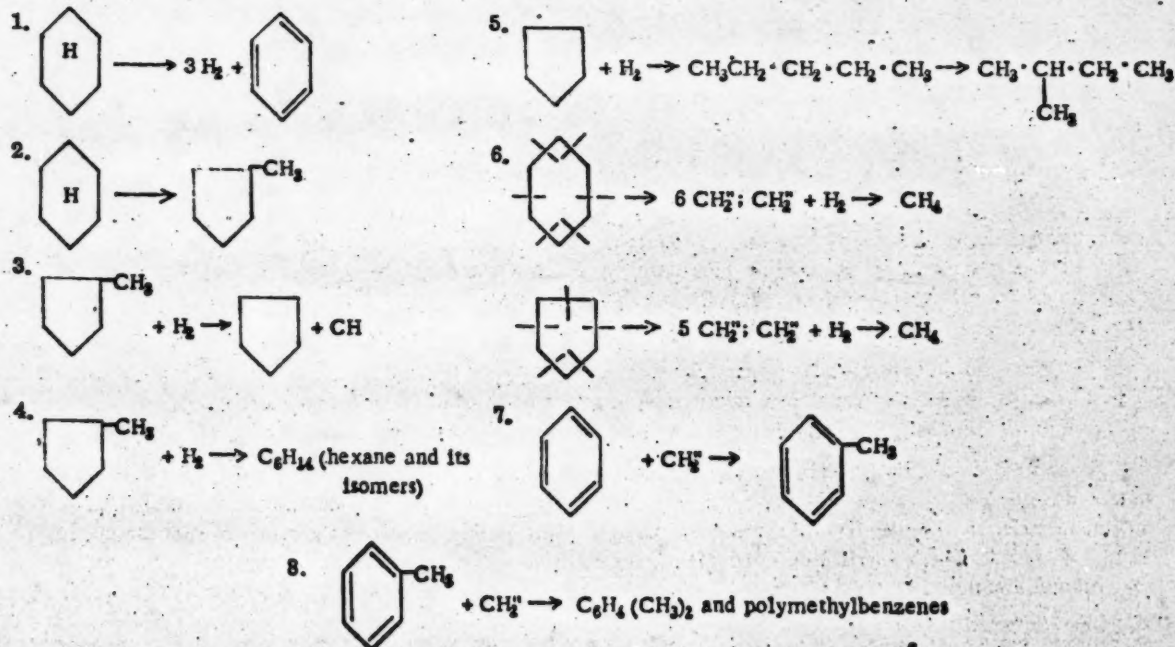
TABLE 6
Fractional Composition of the Aromatic Hydrocarbons of the Cyclohexene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Yield (%)	
		(ml)	(g)			On mixture of hydrocarbons taken for fractionation	On original cyclohexane
1	79.5-80.1	52.0	45.6	1.5010	0.8765	87.7	71.6
2	80.1-110.0	0.15	0.1	—	—	0.2	0.1
3	110-110.5	1.0	0.9	1.4970	—	1.7	1.4
4	110.5-148	1.3	1.0	1.4960	0.8642	1.7	1.4
	Residue	3.5	3.0	1.5480	—	5.7	5.3

Also, the catalyzate contains a small amount of cyclopentane (Fraction 2, Table 5) and of other hydrocarbons having less than six carbon atoms (Fraction 1, Table 5). The results obtained form the basis of the following scheme of the various catalytic reactions of cyclohexane under the given conditions: (see below)

Thus, it has been shown in the present investigation that by the use of a comparatively low pressure of hydrogen, of elevated temperature, and of an active platinum-alumina catalyst, far-reaching changes can be brought about in five- and six-membered cycloalkanes, which have been previously considered

to be comparatively inert, leading to the formation of hydrocarbons of other classes.



SUMMARY

1. It has been found that cyclopentane, under a high pressure of hydrogen (20 atm), in presence of a platinum-alumina catalyst, and at 460°, undergoes far-reaching changes with formation not only of hydrogenolysis products (pentane, and isopentane formed by its isomerization), but also hydrogenosynthesis (methylcyclopentane, hexane and its isomers, benzene, toluene, xylene, polymethylbenzenes).
2. Under similar conditions (hydrogen pressure, 15 atm), methylcyclopentane is converted into a mixture of cyclopentane, pentane, 2-methylbutane, hexane and its isomers, benzene, toluene, xylene, and polymethylbenzenes.
3. In contact with the same catalyst at 460° under a pressure of hydrogen (15 atm), cyclohexane gives a mixture of benzene, methylcyclopentane, cyclopentane, hexanes, pentanes, toluene, xylenes, and polymethylbenzenes.
4. The synthesis reactions are in all cases to be explained by the alkylation of hydrocarbon molecules (cyclopentane, benzene, toluene) by means of methylene radicals arising under the given conditions as a result of the methane breakdown of cycloalkanes at the surface of the specific platinum-alumina catalyst.

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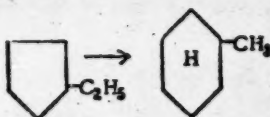
CATALYTIC ISOMERIZATION OF ETHYLCYCLOPENTANE IN THE VAPOR PHASE

N. I. Shuikin and S. S. Novikov

Study by a number of workers [1] of the isomerizing action of aluminum chloride on cyclohexane and methylcyclopentane has shown that these hydrocarbons, when heated in the liquid phase with aluminum chloride, are mutually convertible to an extent that is dependent on conditions. Subsequent investigation by Turova-Polyak and coworkers [2] has shown that not only methylcyclopentane, but also a number of other mono- and di-substituted homologs of cyclopentane are converted under definite conditions of liquid-phase catalysis with the aid of aluminum chloride into the corresponding homologs of cyclohexane. These investigations led Zelinsky, Turova-Polyak, and Gasan-Zade [3] to consider whether the isomerization of the lower homologs of cyclopentane into six-membered cycloalkanes might be applied to analytical purposes. These authors subjected dearomatized Kalin gasoline to the action of aluminum chloride and showed that the most complete isomerization of five-membered to six-membered cycles occurred at 35° in presence of 10% of aluminum chloride, the duration of treatment being 15-18 hours.

The procedure adopted in the investigations that have been carried out have generally been based on treatment of the hydrocarbons under investigation with aluminum chloride at temperatures below their boiling points, i.e., in the liquid phase. However, it would appear, and we have indeed found, that isomerization in the vapor phase is more convenient, for in this way continuous reaction with considerably less expenditure in time is assured.

In pursuance of the question of finding new methods for the catalytic synthesis of methylcyclohexane from petroleum, we have studied this reaction in the first place using pure synthetic ethylcyclopentane. We treated this hydrocarbon with a catalyst consisting of aluminum chloride deposited on activated birch charcoal, and found that at 120°, with space velocity of 0.3, isomerization of ethylcyclopentane into methylcyclohexane proceeds almost quantitatively, in spite of the equilibrium nature of this reaction:



The optimum conditions that we found for the isomerization of pure ethylcyclopentane in the vapor phase to give an enlarged ring were then employed in experiments with narrow fractions of two samples of gasoline containing ethylcyclopentane in admixture with alkanes. We took for investigation an Emben gasoline fraction of b.p. 96-105°, and a Maikop gasoline fraction of b.p. 96-102°, which had been obtained by removal of aromatics (toluene) from the 97-103° fraction of Emben and Maikop gasolines. It was natural to suppose that five-membered cycloalkanes were represented in our gasoline fractions by only ethylcyclopentane (b.p. 103.4°).

The isomerization experiments that we have carried out with these fractions, which are essentially ethylcyclopentane concentrates, have shown that from the sample of Maikop gasoline (fraction of b.p. 96-102°), it is possible to obtain about 43% of methylcyclohexane; the Emben gasoline fraction of b.p. 96-105° gave an isomerizate containing 26.5% of methylcyclohexane. Calculation shows that by making use of vapor-phase isomerization of ethylcyclopentane the content of methylcyclohexane in the 97-103° fraction of Maikop and Emben direct-distillate gasolines can be raised respectively from 35 to 60% and from 50 to 63%.

EXPERIMENTAL

We took for the experiments:

1. Pure synthetic ethylcyclopentane, b.p. 102.5-103.5° (750 mm); n_D^{20} 1.4200 and d_4^{20} 0.7667.
2. The methylcyclohexane fraction of Maikop gasoline having the boiling range 97-103°; n_D^{20} 1.4065 and d_4^{20} 0.7389.
3. The methylcyclohexane fraction of Emben gasoline having the boiling range 97-103°; n_D^{20} 1.4173 and d_4^{20} 0.7470.

In order to free them from cyclohexane hydrocarbons, both fractions were subjected to exhaustive dehydrogenation in presence of platinized charcoal at 300°, and then to treatment with 3% oleum. The

dearomatized residues so obtained had the following properties:

- a) Maikop gasoline fraction: b.p. 96-102°; n_D^{20} 1.4052; d_4^{20} 0.7219.
b) Emben gasoline fraction: b.p. 96-105°; n_D^{20} 1.4015; d_4^{20} 0.7065.

The isomerization catalyst was prepared as follows: some aluminum chloride was placed on the bottom of a porcelain beaker and then covered by a layer of carefully dried activated charcoal (8-10 mm granulation; 24-hour activity to ether, 23.5); the aluminum chloride was then gradually sublimed at 140-145° (bulb of thermometer in charcoal) into the charcoal layer over a period of 40-45 minues with careful periodic stirring. The charcoal, now impregnated with aluminum chloride, was then rapidly transferred to the catalysis tube, which was hermetically sealed and was placed in an inclined electric furnace having a thermoregulator. The original material was supplied to the catalysis tube from an automatic buret, and the catalyzate was collected in a special receiver, cooled with a snow-salt mixture.

Experiment No. 1. Ethylcyclopentane (49.4 g) was passed in a stream of dry hydrogen chloride at 115-120° over the catalyst, which contained 40% of aluminum chloride, at a space velocity of 0.3. The catalyzate obtained (43.2 g), after being washed with water and dried with calcium chloride, had the following properties: b.p. 98-102°; n_D^{20} 1.4216 and d_4^{20} 0.7676. This catalyzate was then dehydrogenated over platinized charcoal at 300°, yielding a condensate that boiled in the range 98-111° and had n_D^{20} 1.4866 and d_4^{20} 0.8570. It was found to contain 92% by weight of toluene, corresponding, as calculation shows, to a 98% conversion of ethylcyclopentane into methylcyclohexane. This condensate was given two successive treatments with 3% oleum. The unabsorbed part, after being washed with water and then dried over calcium chloride, was distilled over sodium, when it boiled in the range 96-102° and had n_D^{20} 1.4162. According to its properties, this residue consisted of unchanged ethylcyclopentane mixed, evidently, with dimethylcyclopentanes, which were not separately investigated owing to lack of material.

Experiment 2. Ethylcyclopentane (30 g) was passed at 145° (other conditions being as before), over a fresh portion of the same catalyst, giving 25 g of condensate having n_D^{20} 1.4214. After dehydrogenation at 300° in contact with platinized charcoal, the catalyzate obtained had n_D^{20} . When this catalyzate was treated with 3% oleum, only 52% by volume of the hydrocarbon taken for analysis went into the acid layer. The results of this experiment show that rise in temperature to 145° greatly diminishes the extent of the isomerization of ethylcyclopentane.

In further experiments with the 96-102° fraction of Maikop gasoline freed from cyclohexane and aromatic hydrocarbons, the aluminum chloride content of the catalyst was varied. The isomerization was carried out at 120° in a stream of dry hydrogen chloride, 75 ml of gasoline being taken for each experiment. The results obtained are given in Table 1.

TABLE 1

AlCl ₃ content of catalyst (%)	Properties of isomerizate		Properties of dehydrogenation product of isomerizate		Toluene content (% by vol.)
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	
9	1.4078	0.7297	1.4243	0.7518	30
20	1.4090	0.7310	1.4253	0.7526	33
33	1.4091	0.7313	1.4360	0.7640	42
43	1.4096	0.7320	1.4364	0.7641	43

The results given in Table 1 show that rise in the aluminum chloride content of the catalyst from 9 to 33% leads to an appreciable increase in the degree of isomerization, whereas further rise up to 43% of aluminum chloride has practically no effect on the

degree of isomerization. In order to find out whether it is possible to use the catalyst repeatedly, three portions, each of 75 ml, of the same Maikop gasoline fraction were passed successively over the 43%-AlCl₃ catalyst, initially fresh. The results obtained are given in Table 2.

It will be seen from these results that a lowering in the activity of the catalyst becomes appreciable only after 225 ml of gasoline has been passed over it.

The subsequent experiments were carried out with the 96-105° fraction of Emben gasoline after removal of six-membered cycloalkanes and aromatic hydrocarbons; the gaseous medium in which the reaction was carried out was varied. The catalyst and other experimental conditions were the same as in preceding experiments. In order to determine the stability of the catalyst, immediately after the first portion (75 ml) of gasoline, a second portion was passed. The results of these experiments are given in Table 3.

TABLE 2

No.	Amt. of gasoline taken (ml)	Properties of isomerizate		Properties of dehydrogenation product of isomerizate		Toluene content (% by vol.)
		n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	
1	75	1.4091	0.7298	1.4368	0.7638	43
2	75	1.4067	0.7294	1.4361	0.7637	42
3	75	1.4062	0.7283	1.4235	0.7502	28

TABLE 3

Gaseous medium	Properties of isomerizate		Properties of dehydrogenation product		
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	% of aromatics
H_2	1.4040	0.7160	1.4251	0.7509	26.0
	1.4019	0.7087	1.4022	0.7110	1.0
CO_2	1.4037	0.7150	1.4244	0.7496	25.0
	1.4022	0.7090	1.4027	0.7116	2.0
N_2	1.4034	0.7160	1.4254	0.7502	26.0
	1.4022	0.7091	1.4025	—	1.5
HCl	1.4038	0.7161	1.4252	0.7561	26.5
	1.4034	0.7154	1.4248	0.7500	25.0

These results show that replacement of hydrogen chloride by H_2 , CO_2 , or N_2 during the first ten hours of the reaction has no significant effect on the degree of isomerization; after this period, however, in an atmosphere of hydrogen, carbon dioxide, or nitrogen, a sharp fall in the

isomerizing action of the aluminum chloride occurs. On the contrary, dry hydrogen chloride definitely helps to maintain the stability of the catalyst.

SUMMARY

1. It has been shown that it is possible to bring about the isomerization of ethylcyclopentane into methylcyclohexane in the vapor phase in contact with aluminum chloride deposited in charcoal with a yield of 92% of the theoretical amount.

2. At a space velocity of 0.3, the optimum temperature for this reaction lies in the range 120-125°.
3. When the isomerization is carried out on petroleum ethylcyclopentane concentrated in the suitable gasoline fraction, the nature of the latter has no significant effect on the course of the isomerization.
4. On the basis of this observation, a method has been found for the catalytic synthesis of methylcyclohexane from petroleum ethylcyclopentane.
5. Dry hydrogen chloride aids in the maintenance of the isomerizing propensity of aluminum chloride deposited on activated charcoal.

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ADDITION REACTIONS OF FLUOROALKENES

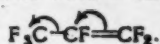
COMMUNICATION 2. ADDITION OF ALCOHOLS AND THIOLS TO PERFLUOROPROPENE

I. L. Knunyants, A. I. Shchekotikhin, and A. V. Fokin

As previously shown, perfluoroalkenes readily undergo addition with nucleophilic reagents in presence of alkalis [1]. The question of the direction of the addition of these substances to perfluoropropene and other perfluoroalkenes has not been considered, because the perfluoro hydrocarbon C_3F_6 , obtained by pyrolysis of polytetrafluoroethylene, has until recently, been assigned the structure of perfluorocyclopropane [2].

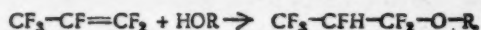
The interaction of the perfluoro hydrocarbon C_3F_6 with hydrogen fluoride and hydrogen bromide has been regarded only from the point of view of a proven cyclopropane structure [3], the structure of the addition products remaining unestablished. Recently, however, study of the infrared spectra of C_3F_6 has shown that it contains a double bond, and in this connection the question arose of the determination of the structures of the addition products formed with various reagents. The solution of this problem as well as the final chemical proof of the structure of the perfluoro hydrocarbon C_3F_6 was also of real theoretical interest.

The trifluoromethyl group has a powerful electron-attracting effect, shown, for example, by the fact that it is 100% meta-directing. Its presence in the molecule of perfluoropropene is bound to have an effect on the polarization of this compound and therefore on the direction of addition of hydrogen-containing substances, in accordance with the electronic basis of Markovnikov's rule:



According to this, the proton of the attacking reagent should add to the middle carbon atom (contrary to propene). Experiment has supported this supposition.

With a view to the more ready identification of the addition products, the smooth reactions of perfluoroalkenes with alcohols and thiols were chosen for study. As was expected, alcohols readily react with perfluoropropene in presence of alkalis with formation of alkyl 2H-hexafluoropropyl ethers:



Thiols react in a similar way with formation of alkyl 2H-hexafluoropropyl sulfides:



As a result of the addition to perfluoropropene of methyl, ethyl, propyl, isopropyl, and butyl alcohols and of phenol, there were obtained in good yields the corresponding methyl, ethyl, propyl, isopropyl, butyl, and phenyl 2H-hexafluoropropyl ethers.

The properties of these compounds are given in Table 1.

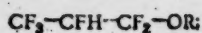
TABLE 1
Properties of Alkyl 2H-Hexafluoropropyl Ethers

No.	Formula	B.p. at norm. press. (°C)	Specific gravity	Refractive index
1	$CF_3-CFH-CF_2-O-CH_3$	54-55	1.429/10°	1.2850/10°
2	$CF_3-CFH-CF_2-O-C_2H_5$	64-65	1.299/20°	1.2960/20°
3	$CF_3-CFH-CF_2-O-(CH_2)_2-CH_3$	92-93	1.260/20°	1.3110/20°
4	$CF_3-CFH-CF_2-O-C_3H_7$	76	1.280/22°	1.3220/22°
5	$CF_3-CFH-CF_2-O-(CH_2)_3-CH_3$	108	1.260/27°	1.3390/27°
6	$CF_3-CFH-CF_2-O-C_6H_5$	95 at 95 mm	1.371/20°	1.3965/20°

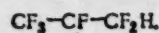
Addition to perfluoropropene of methanethiol, ethanethiol, and 2-mercaptoethanol yielded the corresponding sulfides: methyl, ethyl, and 2-hydroxyethyl 2H-hexafluoropropyl sulfides, the properties of which are given in Table 2.

The direction of addition and the structures of the compounds obtained were determined by the following consid-

erations, which were confirmed by the facts. Addition of alcohols to perfluoropropene can theoretically lead to compounds of two types, I and II:



(I)

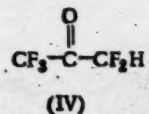
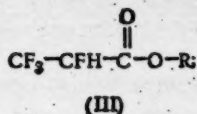


OR (II)

TABLE 2
Properties of Alkyl 2H-Hexafluoropropyl Sulfides

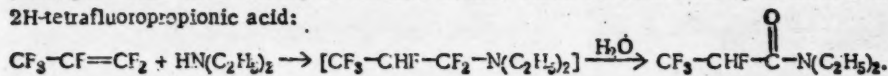
No.	Formula	B.p. at norm. press. (°C)	Specific gravity at 20°	Refractive index at 20°
1	$\text{CF}_3\text{-CFH-CF}_2\text{-S-CH}_3$	87	1.380	1.3443
2	$\text{CF}_3\text{-CFH-CF}_2\text{-S-C}_2\text{H}_5$	101	1.322	1.3548
3	$\text{CF}_3\text{-CFH-CF}_2\text{-S-CH}_2\text{-CH}_2\text{OH}$	54 at 5 mm	1.546	1.3835

When these compounds are hydrolyzed there should be formed: esters of 2H-tetrafluoropropionic acid (III) from compounds of the first type, and pentafluoroacetone (IV) from those of the second type:



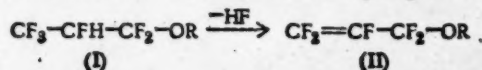
Hydrolysis of the products of addition of alcohols to perfluoropropene, brought about by concentrated sulfuric acid in presence of SiO_2 , which binds hydrogen fluoride, leads exclusively to the formation of esters of 2H-tetrafluoropropionic acid (III). Thus, hydrolysis of 2H-hexafluoropropyl methyl ether and of ethyl 2H-hexafluoropropyl ether yielded respectively the methyl and ethyl esters of 2H-tetrafluoropropionic acid as sole reaction products.

In order to prove the direction of addition of hydrogen-containing substances to perfluoropropene, use was made also of the reaction of fluoroalkenes with alkylamines. Diethylamine, in addition to perfluoropropene, gave what was evidently an unstable amine, which was converted by water into the diethylamide of 2H-tetrafluoropropionic acid:



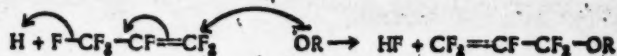
Both the structure of perfluoropropene and the direction of addition to this compound of various hydrogen-containing substances are proved by the fact that these substances are obtained.

In the course of our study of the addition of alcohols to perfluoropropene it was shown that, in addition to alkyl 2H hexafluoropropyl ethers, small amounts of unsaturated compounds were formed, which were readily separated from other reaction products in the form of dibromides. Analysis of the dibromides showed that they were products of the addition of bromine to alkyl perfluoroallyl ethers formed together with alkyl 2H-hexafluoropropyl ethers during the addition of alcohols to perfluoropropene. It was natural to consider that the alkyl perfluoroallyl ethers (II) arose from the alkyl 2H-hexafluoropropyl ethers (I) by the splitting from the latter of hydrogen fluoride under the action of the alkalis catalyzing the reaction:



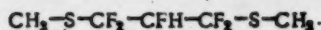
However, negative results obtained in specially designed experiments aiming at the splitting of hydrogen fluoride from alkyl 2H-hexafluoropropyl ethers by the aid of quinoline, alkoxides, alkalis, or potassium fluoride, even under very severe conditions (200°), compelled us to reject the hypothesis. In all cases the original ether remained unchanged, although formation of alkyl perfluoroallyl ethers proceeds during the addition of an alcohol to perfluoropropene at a temperature of only 50-60°. Another possible explanation of the formation of alkyl perfluoroallyl ethers is the direct replacement of one of the fluorine atoms in the trifluoromethyl group by alkoxyl. This explanation, however, is in conflict with the known facts concerning the stability of fluorine in the trifluoromethyl group and with the well known properties of fluoroalkenes.

In the previous communication [1], it was suggested, on the basis of the chemical properties of perfluoroalkenes, that the primary process, determining addition reactions to perfluoroalkenes due to electron depletion of the π -bond of the perfluoroalkene, is an anionoid attack by a nucleophilic reagent, which donates electrons to carbon atoms united by a double bond. The polarizability in the moment of reaction increases the σ , π -conjugation and makes a fluorine atom of the trifluoromethyl group mobile, so that it comes away as an anion:

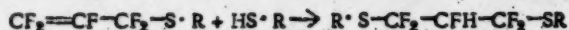
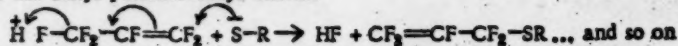


These reaction result in the formation of alkyl perfluoroallyl ethers.

In a similar way, in the addition of thiols to perfluoropropene, there are formed, not only the usual addition products, but also disulfides of the following structure:



The formation of these substances is the result of the further addition of thiols to alkyl perfluoroallyl sulfides formed similarly to the alkyl perfluoroallyl ethers:



The formation of disulfides of this type is a further proof of the correctness of hypotheses advanced, but the question of the mechanism of the formation of alkyl perfluoroallyl ethers and sulfides may be solved finally by a study of the addition of alcohols and thiols to perfluoropropene having labeled carbon atoms.

EXPERIMENTAL

I. Reaction of Alcohols with Perfluoropropene

1. 2H-Hexafluoropropyl methyl ether. Freshly distilled methanol (3.0 g), powdered, fused caustic potash (0.7 g), and condensed perfluoropropene (15 g), were introduced into a 100-cc autoclave of chromium-nickel stainless steel cooled to -70° . The autoclave was maintained at 60° for 13 hours with constant rotation, and was then cooled to -70° . Unchanged perfluoropropene (0.4 liter, i.e. 2.6 g) was driven off, and a liquid distillate (16.4 g) then came over at $44-53^\circ$. The crude ether was brominated by the method described in the next section, and a fraction was then obtained having a b.p. of $52-55^\circ$ (14.2 g, 83% of perfluoropropene taken for reaction). Redistillation yielded a substance of b.p. $54-55^\circ$, which appeared to be pure 2H-hexafluoropropyl methyl ether. It was a colorless mobile liquid of pleasant odor: d_4^{20} 1.429; n_D^{20} 1.2850; calculated MR 23.09; found MR 22.30.

Found %: F 62.4; M 176 (cryoscopic)

$\text{C}_4\text{H}_2\text{OF}_6$. Calculated %: F 62.6; M 182

2. 2,3-Dibromopentafluoropropyl methyl ether. The fraction of b.p. $44-53^\circ$ (15.7 g), the mixture of saturated and unsaturated ethers obtained by the method described in the first section, was placed in a test tube cooled with ice water and provided with reflux condenser and with a buret, from which bromine was slowly added. When decolorization ceased, a further amount of bromine was added, the reaction mixture was set aside for thirty minutes at room temperature, and it was then washed with saturated thiosulfate solution and with water. The product was dried over anhydrous magnesium sulfate and was fractionated (17 g). The following fractions were separated:

Fraction I, b.p. $52-55^\circ$; 14.2 g

Fraction II, b.p. $128-136^\circ$; 1.5 g

Fraction II, b.p. $128-136^\circ$, boiled after redistillation at 136° (2,3-dibromopentafluoropropyl methyl ether). This compound is a colorless liquid having a terpene-like odor: d_4^{20} 1.900; n_D^{20} 1.3700; found MR 38.40; calculated MR 37.65.

Found %: Br 48.6

$\text{C}_4\text{H}_2\text{F}_5\text{Br}_2$. Calculated %: Br 49.8

3. Ethyl 2H-hexafluoropropyl ether. Absolute ethanol (3.0 g), powdered fused caustic potash (0.8 g), and perfluoropropene (13.4 g, i.e. 37% excess) were introduced into a 100-cc autoclave of chromium-nickel stainless steel cooled to -70° . The autoclave was maintained at $50-60^\circ$ for 14 hours with constant rotation, and was then cooled to $-60-70^\circ$. Unchanged perfluoropropene (0.7 liter, i.e. 4.55 g), was driven off, and a liquid distillate (11.0 g, 92.7% of perfluoropropene taken for reaction), then came over at $57-65^\circ$. After treatment with bromine in the usual way (see Section 2), the crude product (12.9 g) was fractionated, the $64-65^\circ$ fraction, i.e., ethyl 2H-hexafluoropropyl ether (9.4 g, 79.3%), being collected. It was a clear mobile liquid of pleasant odor; d_4^{20} 1.299; n_D^{20} 1.2960; found MR 27.90; calculated MR 27.71.

Found %: F 57.6; M 190 (cryoscopic)

$\text{C}_3\text{H}_5\text{OF}_6$. Calculated %: F 58.2; M 196

4. 2H-Hexafluoropropyl propyl ether. Freshly distilled propyl alcohol (11.6 g), powdered fused caustic potash (0.9 g), and condensed perfluoropropene (8.4 g) were introduced into a 100-cc autoclave. The autoclave was heated at 55-60° with constant rotation for 16 hours, and was then cooled to -70°. Unchanged perfluoropropene was driven off (0.2 liter, i.e. 1.3 g). Fractionation of the residue yielded:

Fraction I, b.p. 75-89°;	6.5 g.
Fraction II, b.p. 89-98°;	4.0 g.
Residue	4.5 g.

Fraction II (mainly alcohol), was washed several times with water and then dried over anhydrous magnesium sulfate, thus giving a further 1.9 g of product, which was added to Fraction I. The crude ether was treated with bromine by the method described in Section 2, and the saturated propyl ether was distilled from the dibromo compound at 90-93°, yielding practically pure 2H-hexafluoropropyl propyl ether (6.1 g), b.p. 92-93°. It was a clear, colorless mobile liquid of pleasant odor: d_4^{20} 1.260; n_D^{25} 1.3110; found MR 32.0; calculated MR 32.30.

Found %: F 54.4
 $C_6H_5OF_6$ Calculated %: F 54.3

5. 2H-Hexafluoropropyl isopropyl ether. Freshly distilled isopropyl alcohol (10.7 g), powdered fused caustic potash (0.7 g), and perfluoropropene (32.6 g, 20% excess) were introduced into an autoclave cooled to -70°. The autoclave was heated to 55-60° with constant rotation for 20 hours, and was then cooled to -70°. Unchanged perfluoropropene was driven off (2.69 liter, i.e. 17.6 g). Fractionation of the remainder (16 g), gave the following fractions:

Fraction I, b.p. 65-75°;	6.5 g.
Fraction II, b.p. 75-84°;	6.5 g.
Residue	2.8 g.

Fraction II was washed several times with cold water and was dried over anhydrous magnesium sulfate, yielding a further 2.3 g of product, which was added to Fraction I. Refractionation yielded a fraction of b.p. 65-76° (8.5 g, 40.5%). This fraction was treated with bromine in the usual way (see Section 2). The saturated 2H-hexafluoropropyl isopropyl ether was distilled from the dibromo compound at 76° (3.6 g, 17.1%). It was a clear, colorless, mobile liquid of pleasant odor: b.p. 76°; d_4^{22} 1.280; n_D^{22} 1.3220; found MR 31.83; calculated MR 32.50.

Found %: F 53.2.
 $C_6H_5OF_6$ Calculated %: F 54.3.

6. Butyl 2H-hexafluoropropyl ether. Freshly distilled butyl alcohol (12.8 g), powdered fused caustic potash (1.4 g), and condensed perfluoropropene (12 g) were introduced into a autoclave cooled to -70°. The autoclave was heated at 55-60°, with constant rotation for 18 hours, and then cooled to -70°. The autoclave was opened, and unchanged perfluoropropene was driven off (0.74 liter, i.e. 4.9 g), and a liquid-condensate (19.9 g) was also obtained. Fractionation of the latter yielded:

Fraction I, b.p. 82-90°;	1 g
Fraction II, b.p. 105-110°;	10.1 g.
Fraction III, b.p. 110-118°;	5.7 g.
Residue	3.1 g

Fraction II (b.p. 105-110°) was boiled in a flask under reflux in presence of sodium, in order to remove alcohol; it was then fractionated, the 105-109° fraction being collected. After bromination, the saturated butyl 2H-hexafluoropropyl ether was distilled from the dibromo compound at 108° (3.6 g, 34%). It was a colorless, mobile liquid of pleasant odor: b.p. 108°; d_4^{27} 1.270; n_D^{27} 1.3360; found MR 36.90; calculated MR 37.05.

Found %: F 49.3.
 $C_7H_{10}OF_6$ Calculated %: F 50.9.

7. 2H-Hexafluoropropyl phenyl ether. Freshly distilled phenol (10.8), powdered fused caustic potash (0.7 g), and liquid perfluoropropene (13.3 g) were introduced into an autoclave cooled to -70°. The autoclave was hermetically sealed and heated at 50°, with constant rotation for 10 hours, and was then cooled to -70°. Unchanged perfluoropropene (0.24 liter, i.e. 1.6 g), was driven off, and the reaction mixture (22 g) was washed

with 10% caustic alkali to remove unchanged phenol. It was then extracted with ether, and the ether solution was washed with water and dried over calcium chloride. The ether was removed, and the residue was vacuum-fractionated. The main fraction boiled at 92-94°/93 mm. Redistillation yielded practically pure 2H-hexafluoropropyl phenyl ether, b.p. 95°/95 mm (44.7% yield). It was a clear, colorless liquid of pleasant odor: d_4^{20} 1.371; n_D^{20} 1.3965; found MR 42.60; calculated MR 42.58.

Found %: F 45.9.

$C_9H_5F_6O$. Calculated %: F 46.8.

II. Hydrolysis of Alkyl 2H-Hexafluoropropyl Ethers into Alkyl Esters of 2H-Tetrafluoropropionic Acid

8. Methyl 2H-tetrafluoropropionate. Sulfuric acid of sp. gr. 1.84 (10 g), and 11.8 g 2H-hexafluoropropyl methyl ether of b.p. 52-55°, were introduced into an autoclave of chromium-nickel stainless steel cooled in a mixture of ice and common salt. Powdered glass (2.2 g), was added for binding hydrogen fluoride. The autoclave was hermetically closed and was heated at 60-65° with constant rotation for three hours.

The autoclave was then cooled, and the reaction mixture was carefully poured into ice water, when layers were formed. The lower, ester layer, which had a yellowish color, was separated, washed with a saturated solution of bicarbonate and then water and dried over freshly roasted magnesium sulfate. The aqueous layer was extracted with ether, and the ether extract was dried over magnesium sulfate. The ether was removed and the main product was added to the residue in the distilling flask. Distillation yielded methyl 2H-tetrafluoropropionate (6.9 g, 65.6%), a colorless liquid having a characteristic odor: b.p. 96°; d_4^{20} 1.353; n_D^{20} 1.3192; found MR 23.27; calculated MR 22.73.

Found %: F 46.3; M 157 (cryoscopic).

$C_4H_4O_2F_4$. Calculated %: F 47.5; M 160.

9. Ethyl 2H-tetrafluoropropionate. Sulfuric acid of sp. gr. 1.84 (10 g), ethyl 2H-hexafluoropropyl ether of b.p. 64-65° (15.0 g), and powdered glass for binding hydrogen fluoride (2.3 g), were introduced into an autoclave cooled by a mixture of ice and common salt. The autoclave was heated at 75°, with constant rotation for three hours, and was then cooled. The reaction mixture was carefully poured into ice water, when layers were formed. The lower layer was separated, washed with a saturated solution of bicarbonate and with water, and dried over freshly roasted magnesium sulfate. The aqueous layer was extracted with ether, and the ether extract was dried over magnesium sulfate. The main product was added to the residue remaining in the distillation flask after removal of ether, and fractionation yielded ethyl 2H-tetrafluoropropionate (7.9 g, 59.4%), a colorless, mobile liquid of characteristic odor: b.p. 108-109°; d_4^{20} 1.289; n_D^{20} 1.3260; found MR 27.19; calculated MR 26.86.

Found %: F 42.8; M 169 (cryoscopic).

$C_5H_6O_2F_4$. Calculated %: F 43.7; M 174.

III. Addition of Thiols to Perfluoropropene

10. 2H-Hexafluoropropyl methyl sulfide. Methanethiol (10.5 g), perfluoropropene (33 g), and dry caustic soda (1 g), were introduced into a 70-cc steel autoclave. The autoclave was heated for six hours at 120-140°. It was then cooled, and unchanged perfluoropropene was driven off (2 liters). A liquid product was extracted from the autoclave (12 ml) and was fractionated; refractionation yielded:

Fraction I, b.p. 85-87° 7.5 g;

Fraction II, b.p. 72°/32 mm, 2 g.

2H-Hexafluoropropyl methyl sulfide is a clear, colorless liquid, having a sharp, unpleasant odor: d_4^{20} 1.380; n_D^{20} 1.3443; found MR 30.40; calculated MR 29.37, b.p. 87°.

Found %: S 15.80; F 55.3.

$C_4H_4SF_6$. Calculated %: S 16.10; F 57.50

11. Ethyl 2H-hexafluoropropyl sulfide. Ethanethiol (12.5 g), perfluoropropene (30 g), and dry caustic soda (1 g) were introduced into a 70-cc autoclave. The autoclave was heated for six hours at 120-140° with constant rotation. It was then cooled, and unchanged perfluoropropene was driven off (2 liters). The crude product (21 g) was fractionated. Refractionation yielded the fractions:

Fraction I, b.p. 100-102°/752 mm, 17 g (34%).

Fraction II, b.p. 50-52°/100 mm, 3.5 g.

After redistillation, Fraction I boiled at 100-101°.

Ethyl 2H-hexafluoropropyl sulfide is a clear, colorless liquid of unpleasant odor: d_4^{20} 1.322; n_D^{20} 1.3548; found MR 34.93; calculated MR 33.991.

Found %: S 14.30; F 49.22.

$C_5H_6SF_6$. Calculated %: S 15.10; F 53.80.

Refractionation of Fraction II yielded as main product a liquid of b.p. 89-90°/140 mm, which appeared to be practically pure disulfide. It was a clear, yellow liquid having a specific odor: b.p. 89-90°/140 mm: d_4^{20} 1.294; n_D^{20} 1.4045. Found MR 49.03; calculated MR 50.56.

Found %: S 24.80; F 38.1.

$C_4F_5S_2H$. Calculated %: S 25.30; F 37.6

12. 2H-Hexafluoropropyl 2-hydroxyethyl sulfide. 2-Mercaptoethanol (10 g), perfluoropropene (20 g), and dry caustic soda (0.8 g) were introduced into a steel cylinder, 70 cc in volume. The hermetically closed cylinder was heated for six hours at 100-120° and then cooled. It was then opened, and unchanged perfluoropropene was driven off. The crude product was washed with alkali and extracted with ether. The ether extract was dried overnight with magnesium sulfate, the ether was driven off, and the residue was vacuum-fractionated, a fraction of b.p. 53-54°/5 mm being separated. It was 2H-hexafluoropropyl 2-hydroxyethyl sulfide (6 g, 20.5%), a clear, colorless liquid of pleasant odor; it has d_4^{20} 1.546; n_D^{20} 1.3835; found MR 34.5; calculated MR 35.51.

Found %: S 14.60.

$C_5H_6OSF_6$. Calculated %: S 14.05

13. Addition of diethylamine to perfluoropropene. Diethylamine (10 g), perfluoropropene (20 g), and borax (1 g) were introduced into a 70-cc stainless-steel cylinder. The hermetically sealed cylinder was heated for four hours at 90°, and the cylinder was then cooled to -70°. Unchanged perfluoropropene was driven off, and the residual liquid was washed with water, extracted with ether, and dried with magnesium sulfate. The product was then vacuum-fractionated, the fraction of b.p. 89°/22 mm, the diethylamide of 2H-tetrafluoropropionic acid, being separated. It was a clear, colorless liquid of unpleasant odor: d_4^{20} 1.228; n_D^{20} 1.3910; found MR 38.92; calculated MR 38.39.

Found %: F 38.8; N 6.80

$C_7H_{11}F_4ON$. Calculated %: F 37.9; N 6.95

SUMMARY

1. Perfluoropropene, in presence of alkalis, readily unites with alcohols and thiols, and the hydrogen atom of the hydroxyl group of the alcohol or of the mercapto group of the thiol, in contrast to its behavior, in the case of propene, adds to the middle carbon atom of perfluoropropene.
2. The alkyl 2H-hexafluoropropyl ethers formed as a result of reaction of perfluoropropene with alcohols are readily hydrolyzed into esters of 2H-tetrafluoropropionic acid (proof of direction of addition).
3. The normal addition reaction, leading to formation of alkyl 2H-hexafluoropropyl ethers, is accompanied by the formation in appreciable amount of alkyl perfluoroallyl ethers (or alkyl perfluoroallyl sulfides in the case of reaction with thiols).
4. It has been established that the fluorine atoms of the trifluoromethyl group of perfluoropropene, unlike those in compounds carrying a trifluoromethyl group on an atom not linked to a neighbor by a multiple bond, have an appreciable degree of mobility.
5. The formation of perfluoroallyl derivatives in reactions of perfluoropropene with substances containing mobile hydrogen atoms (alcohols, thiols, etc.) cannot be regarded as a direct replacement of a fluorine atom of the trifluoromethyl group (by alkoxyl or alkylthio), but is the result of anionoid attack by a nucleophilic reagent on the extreme carbon atom of perfluoropropene having the least electron density: in the moment of attack, transposition of the double bond occurs, and one of the fluorine atoms of the trifluoromethyl group is removed as an anion.

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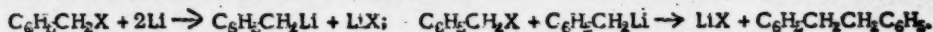
• See Consultants Bureau English translation, page 279.

CRYSTALLINE ORGANOLITHIUM COMPOUNDS. BENZYLITHIUM

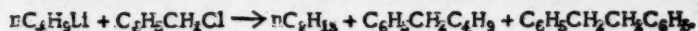
T. V. Talalaeva and K. A. Kocheschkov

Benzylithium, being the simplest aralkyl organolithium compound, is of considerable interest: its properties differ from those of the aliphatic and aromatic compounds in the direction of increased reactivity (which is made use of mainly for analytical purposes) [1]. It is probable that this increased reactivity also explains why there have been no satisfactory methods up to the present for the preparation of benzylithium in a pure form, either in solution, or in the isolated, solid (crystalline) state. Actually, the usual methods for the synthesis of organolithium compounds are of little applicability in this case.

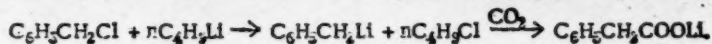
Thus, when benzyl halide is treated directly with lithium, the reaction does not stop at the organolithium-compound stage, because a further condensation reaction with benzyl halide rapidly sets in with formation of dibenzyl [2]:



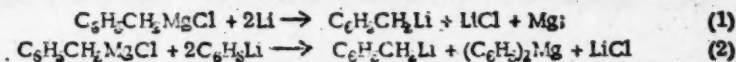
The double-decomposition reaction between organolithium compounds and benzyl halides is more complex than this:



These condensations proceed so readily that it is possible to demonstrate the intermediate formation of benzylithium only indirectly: reaction of benzyl chloride with butyllithium at -50° followed by carboxylation with solid carbon dioxide gives a small amount of phenylacetic acid [3]:

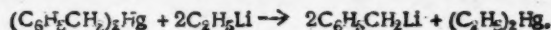


The double-decomposition reactions between organomagnesium compounds and lithium or RLi are of considerable interest:



However, both of these reactions, apart from the fact that they proceed extremely slowly and do not give consistently reproducible results, always yield a mixture of benzylithium, organomagnesium compound, and lithium salt [4].

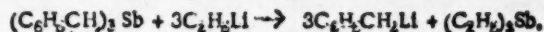
Finally, experiments have been described on the isolation of benzylithium by means of the double-decomposition reaction between dibenzylmercury and ethyllithium:



This method also has great drawbacks and could not be applied as a convenient synthesis of benzylithium. There were difficulties in the preparation of large amounts of the starting materials, both of pure dibenzylmercury, and also of ethyllithium; for, until recently, this was synthesized from diethylmercury and lithium. A further drawback was the formation in this reaction of the highly toxic diethylmercury.

The authors who described this method could not obtain sufficient quantities of benzylithium, and also, evidently, did not obtain a completely pure product, for it was greasy and did not come away from the walls. The benzylithium was analyzed by decomposing the whole amount by alcohol in a filtration apparatus; the yield of benzylithium was not indicated [5].

As indicated in a previous communication [6], we have developed a convenient method for the preparation of pure crystalline ethyllithium by the reaction of ethyl bromide (or chloride) with lithium, so avoiding the highly toxic mercury compounds that were used previously. This enabled us to make a closer investigation of the double-decomposition reactions of ethyllithium with organometallic compounds of other metals, in particular antimony [7]. This procedure has been applied also to the synthesis of benzylithium:



The preparation of pure benzylithium presents certain experimental difficulties owing to its low

stability and high reactivity. It is necessary to work with pure starting materials (tribenzylantimony, ethyllithium), in dry solvents (pentane, thiophene-free benzene), in an atmosphere of pure dry nitrogen, and in special apparatus permitting isolation from moisture and atmospheric oxygen [7].

It is of interest to note that at reaction temperatures of above 40° the color of solution and precipitate changes considerably, becoming orange and then, with further rise in temperature, brownish red. A similar change has been observed previously by Hein and coworkers [5] and was erroneously attributed to the formation of "reddish-violet lithium compounds of the same type as disodiumstilbene $C_6H_5CHNa-CHNaC_6H_5$ ". When the reaction was carried out at 65-75° with an excess of ethyllithium, we isolated, in quantitative yield, a brownish-red crystalline compound corresponding accurately in analysis to the formula $C_7H_6Li_2$. A compound of the type $C_6H_5CHLi-CHLiC_6H_5$ would contain half as much lithium.

Tribenzylantimony, in the form of a snow-white, finely crystalline powder, was prepared under nitrogen in an apparatus having ground joints by the action of antimony trichloride on benzylmagnesium chloride. The method for the preparation of tribenzylantimony described by Tsukervanik and Smirnov [8], in which apparatus similar to that used in the synthesis of tribenzylarsenic [9] is used, is less convenient.

EXPERIMENTAL

Preparation of Tribenzylantimony. The preparation of an ether solution of benzylmagnesium chloride was carried out in a one-liter three-necked flask attached by ground joints to reflux condenser, dropping funnel, stirrer with mercury seal, and source of pure dry nitrogen. The condenser was connected to a Tishchenko vessel containing concentrated sulfuric acid. Iodine-activated magnesium (8.1 g, i.e. 0.33 g-atom) and absolute ether (200 ml) were introduced into the nitrogen-filled flask. Some benzyl chloride (about 5 ml) was added to initiate the reaction, and the remaining amount was diluted with 100 ml of absolute ether and added gradually so as to maintain a vigorous boil, about 35 minutes being required (total amount added, 42.4 g, i.e. 0.33 mole). Boiling was continued for a further 15 minutes, and the flask was then cooled with ice (the nitrogen stream being maintained).

Then, with cooling and good stirring, a solution was added of antimony trichloride (22.8 g; 0.1 mole) in absolute ether (100 ml) over a period of 10-15 minutes. When the addition was complete, the contents of the flask consisted of a fairly thick light-gray mass. While nitrogen continued to pass, the flask was rapidly disconnected from the stirrer and closed with a stopper; the condenser was removed and the reaction mixture was poured, while nitrogen continued to pass, into a large, closed funnel of 0.75 liter capacity for filtration under nitrogen through a porous glass filter. The funnel and receiver for the filtrate had been carefully dried previously and were full of nitrogen. The funnel was closed, and filtration proceeded under a pressure of nitrogen. Precipitate remaining on the walls of the flask was washed off with a small amount of absolute ether and was also rapidly transferred to the filter. The precipitate on the filter was washed four times with absolute ether (50-ml portions); the filtrate, which was somewhat turbid, was left under nitrogen until the next day. It was then filtered under nitrogen through a dry, folded filter paper into a two-necked nitrogen tube connected with condenser and receiver filled with nitrogen. Ether was then distilled off under nitrogen until the volume was about 40 ml. The nitrogen tube was disconnected from the condenser and cooled to room temperature, while nitrogen continued to pass; pentane (30 ml) was then added, and the mixture was cooled with ice. The fine snow-white crystals that appeared were filtered off under a pressure of nitrogen, washed three times with pentane, dried in a stream of nitrogen, and sealed in ampoules. The yield was 50-55%. The melting point of tribenzylantimony was determined in a capillary tube sealed under nitrogen. The value found was 87°, the value given in the literature being 85-90° [8].

For analysis [10] the substance was sealed in ampoules under nitrogen in amounts of about 0.2-0.4 g. An ampoule was weighed, opened, and reweighed rapidly after substance had been poured out into a Kjeldahl flask.

Found %: Sb 31.14; 30.71

$C_{21}H_{21}Sb$. Calculated %: Sb 30.57

Preparation of Crystalline Benzylolithium. A solution of tribenzylantimony was prepared by rapidly opening an ampoule of tribenzylantimony, connecting it in a countercurrent of nitrogen by a piece of flexible stout-walled rubber tubing to the apparatus, and transferring the substance. Solvent was then added, and the mixture was warmed slightly (and if cloudy was filtered in an atmosphere of nitrogen through folded filter paper that had been dried over phosphoric oxide) [7]. All operations of uniting apparatus were carried out rapidly and in such

a manner that the solutions were continuously protected by the passing stream of pure dry nitrogen. The cylinder nitrogen (oxygen content not greater than 0.3%) was purified by passing through three columns of the same length containing calcium chloride, caustic potash, and phosphoric oxide on glass wool respectively.

A clear solution of tribenzylantimony (9.5 g; 1 mole) in a mixture of dry thiophene-free benzene (50 ml) and pentane (50 ml) was introduced into the special apparatus [7], which had been dried out and filled with nitrogen; the mixture was cooled to 0°. A clear, benzene solution (44.3 ml) of ethyllithium (2.59 g; 3 moles) was then added from a buret through the upper exit of the apparatus, and the apparatus was closed, the reaction mixture being left overnight at 0°. The yellow color of benzyllithium appeared shortly after the solutions were mixed; a cloudiness then appeared, and a fine, lemon-yellow precipitate of benzyllithium began to come down: it readily formed large flakes, which gradually settled on the walls of the apparatus. When the reaction was carried out at room temperature, it was practically complete in one to two hours. When ethyllithium was added to the tribenzylantimony solution warmed to 30-35°, or when the reaction mixture was warmed to this temperature, the reaction was complete in 20-30 minutes. In order to filter off the precipitate of benzyllithium, a filtration apparatus having a porous glass filter [7], previously dried and filled with nitrogen, was connected to the side exit of the apparatus (the solution being protected by the passing stream of nitrogen). Nitrogen was passed through the apparatus for five minutes, and during this time the precipitate of benzyllithium was cleaned off the walls by means of a rod applied through the upper opening of the apparatus, the lumps, if any had formed, being broken up. The apparatus was closed and inverted; the precipitate was filtered. The receiver for the filtrate was connected to a drying system. The remains of the precipitate were washed out of the apparatus with a small amount of pentane, and the first apparatus was disconnected, leaving the filtration apparatus connected through a side tube to the nitrogen stream, which maintains a small pressure of nitrogen in the apparatus. Through the upper opening (opened for only a short time) the residue was washed on the filter with three successive 20-ml portions of dry pentane, and was then stirred with a rod and, with the apparatus inclined on its side, dried in the stream of nitrogen (passing from the side tube through the filter), with occasional shaking. The receiver containing the filtrate was disconnected.

In order to obtain a dry, readily flowing preparation of benzyllithium, it was dried for about 1-1.5 hours, and the so-obtained lemon-yellow powder of benzyllithium was generally transferred through the side tube of the apparatus to a large ampoule (filled with nitrogen) for weighing and dissolution; at the same time, two or three samples for analysis were taken.

Ampoules containing samples for analysis must not be allowed to lie: analysis must be performed without delay. The same method of analysis was used as in the case of crystalline aromatic lithium compounds [7].

The preparation obtained at 0° gave, on analysis, 7.18-7.22% of lithium, and that obtained at room temperature gave 7.4-7.5% (calculated for C_7H_7Li , 7.08%). Analysis of solutions of benzyllithium was carried out by the usual method (double titration) [11].

The benzyllithium obtained (3.8-4.2 g, 50-56%) was used immediately for further reactions or was dissolved in ether. If a turbid solution was obtained, it was filtered under nitrogen and then sealed in ampoules. Benzyllithium may be preserved in the dissolved state for several days, but, in the dry state (under nitrogen, of course), it changes color and conglomerates even in one day.

SUMMARY

1. Crystalline benzyllithium has been prepared by the reaction of tribenzylantimony with ethyllithium in pentane-benzene solution. Its properties have been investigated.

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* See Consultants Bureau English translation, page 113.

RAMAN SPECTRA OF SOME SILA-HYDROCARBONS

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Developments in the field of organosilicon compounds have presented investigators with a number of problems in the study of their chemical and physical properties, particularly the problem of the structures of these compounds. Organosilicon compounds generally differ in their properties from their hydrocarbon analogs, and the question arises of the extent to which they differ in molecular structure from the corresponding hydrocarbons.

In the solution of structural problems relating to hydrocarbons, great assistance has been given by studies of their vibrational spectra by methods of infrared and Raman spectroscopy. It is natural, therefore, to apply these methods also in the investigation of the structure of organosilicon compounds. Also, the vibrational spectrum being an exactly defined characteristic of a chemical compound (by frequencies, intensity, and state of polarization of the spectral lines), is of great assistance when carrying out molecular-spectrum analysis. Such analysis has already gained a secure place in organic chemistry, for it permits the solution of many analytical problems which cannot be solved by the available methods of chemical analysis. In the literature there are comparatively few papers devoted to the study of the Raman and infrared spectra of organosilicon compounds.

We have undertaken a study of the Raman spectra of organosilicon compounds. In this paper we give the results of a study of the Raman spectra of silanes having ethyl and methyl substituents, the following compounds being investigated:

1. Trimethylsilane ($\text{CH}_3)_3\text{SiH}$. Prepared from trichlorosilane and methylmagnesium bromide; b.p. 10.0-10.5° (b.p. 9-11° [1]).
2. Tetramethylsilane ($\text{CH}_3)_4\text{Si}$. Prepared from silicon tetrachloride and methylmagnesium bromide; b.p. 26°, d_4^{20} 0.6411; n_D^{20} 1.3578; found MR 30.11; calculated MR 30.28 [2]. Literature data b. p. 26-26.5° [3, 4, 5]; d_4^{20} 0.646 [5]; 0.6480 [4]; n_D^{20} 1.3591 [4].
3. Ethyltrimethylsilane ($\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)$. Prepared from trichloroethylsilane and methylmagnesium bromide; b.p. 62-62.5°, d_4^{20} 0.6851; n_D^{20} 1.3818; found MR 34.64; calculated MR 33.91 [2]. Data in the literature: b.p. 62°/760 mm; d_4^{20} 0.6849; n_D^{20} 1.3820 [6].
4. Diethyldimethylsilane ($\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$. Prepared from dichlorodiethylsilane and methylmagnesium bromide; b.p. 95.5°, d_4^{20} 0.7168; n_D^{20} 1.4010; found MR 39.32; calculated MR 39.54 [2]. Data in the literature: b.p. 95.7-96.2°/760 mm; d_4^{20} 0.7168 [7].
5. Triethylmethylsilane ($\text{CH}_3\text{Si}(\text{C}_2\text{H}_5)_3$). Prepared from trichloromethylsilane and ethylmagnesium bromide; b.p. 127°, d_4^{20} 0.7470; n_D^{20} 1.4160; found MR 43.67; calculated MR 44.17 [2]. Data in the literature: b.p. 127° at 760 mm; d_4^{20} 0.7473; n_D^{20} 1.4160 [6].

The Raman spectra of trimethylsilane, ethyltrimethylsilane, diethyldimethylsilane, and triethylmethylsilane were investigated for the first time. The spectrum of tetramethylsilane has already been described in the literature [8].

The Raman spectra of the substances investigated were photographed in a glass three-prism spectrograph (with a camera of $f = 270$ mm). The substance, which was contained in a cylindrical glass cell having a blackened "horn" at its end, was illuminated by the light of a PRK-2 quartz mercury lamp in an illuminating assembly (single-bulb illuminator with elliptical mirrors). The excitation was effected by radiation of $\lambda = 4358$ Å. The violet part of the mercury spectrum was absorbed by a filter (saturated solution of sodium nitrite in water: a 2-cm layer). The spectra were photographed on highly sensitive plates, the time of exposure being 2-3 hours. The Raman frequencies of the substances that we investigated are given in Table 1, in which there are given also the data from the literature on tetramethylsilane [8] and tetraethylsilane [9].

TABLE 1

Raman Frequencies of the Investigated Ethyl- and Methyl-substituted Silanes (cm^{-1})

$\text{HSi}(\text{CH}_3)_3$	$\text{Si}(\text{CH}_3)_4$		$(\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)$	$(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$	$(\text{CH}_3)\text{Si}(\text{C}_2\text{H}_5)_3$	$\text{Si}(\text{C}_2\text{H}_5)_4$ Anderson [9]
		Rank and Bordner [8]				
			155(5)	141(2) 165(2)	185(4)bd	160
219(10)	199(10)b	202	212(10)b	215(5)	237(4)bd	249
251(1)	243(10)b	239	237(8)sh	237(1)d	279(2)d	303
			330(8)sh	299(4) 330(2) 358(2)	301(5) 330(2)	
			433(0)d		372(2)	393
600(5)						
623(20)	590(20)sh*	598	580(20)sh*	558(20)sh* 577(1)	559(20)*	553*
			664(8)sh	653(4)d	646(5)d	625
	690(10)b	696	690(10)	680(3)	678(2)d	
718(8)			750(1)d	704(3)	743(5)d	736
			770(1)d	776(3)d	791(2)d	
839(1)			833(3)d	825(1)d		
908(1)	859(7)b	863	860(1)d		869(0)	865
				907(0)	909(0)	
				947(0)	950(0)	
			969(3)	972(6)	969(7)	978
			1013(5)	1009(6)sh	1009(7)b	1021
						1200
			1230(1)d	1230(4)	1228(5)d	
	1249(2)d		1249(3)d	1247(1)	1246(1)	
1258	1260(2)d	1264				
1414	1418(7)d	1427	1411(8)	1406(8)	1410(8)d	1423
			1461(5)	1458(8)	1461(10)d	1467
2118(10)				2735(2)	2735(2)	2734
						2813
			2881(20)b	2880(20)b	2881(20)b	2885
2902(10)	2898(20)b	2905	2897(20)b	2904(20)b	2899(20)b	2912
				2944(1)		
2967(10)	2957(20)b	2963	2957(20)b	2959(20)b	2958(20)b	2950

Note: In parentheses are given the relative intensities, as estimated visually, of the lines, the intensity of the 1246 cm^{-1} line in the spectrum of triethylmethylsilane being taken as unity.

The symbols used are: b, broad; sh, sharp; d, diffuse.

In the present stage of the investigation it is not possible to give a full interpretation of the spectra of these substances. A fairly full interpretation has been given only of the spectrum of tetramethylsilane, following the analogy with the spectrum of tetramethylmethane [10]. In the spectra of the organosilicon compounds that we have investigated, as in the spectra of hydrocarbons, there are frequencies attributable to the valency and

TABLE 2

Frequencies of C-H Valency Vibrations

Isobutane [1]	Trimethyl- silane	Tetra- methyl- methane [8]	Tetra- methyl- silane	2,2-Dimethyl- butane [12]	Ethyltri- methyl- silane	3,3-Dimethyl- pentane	Diethyl- dimethyl- silane	3-Ethyl-3- methyl- pentane [12]	Triethyl- methyl- silane
2628		2712		2713		2674		2663	
2718		2745		2739		2712		2734	
2778		2794		2855		2736	2735	2857	2735
2868		2864		2870	2881	2855		2883	2881
2906	2902	2892	2898	2893	2897	2864	2880	2897	
2936		2911		2904		2890	2904	2915	2899
2959		2937		2942		2907		2932	
	2967	2955	2957	2963	2957	2942	2944	2943	
						2967	2959	2966	2957

deformation vibrations of the methyl group. Frequencies in the region $1230-1260\text{ cm}^{-1}$ are those due to the vibration of the methyl group, and the frequency of about 1415 cm^{-1} relates to the deformation vibration of H-C-H of the CH_3 group; the frequency of about 1460 cm^{-1} is that of the deformation vibration of H-C-H of the CH_2 group.

In the region of high displacements ($2700-3000\text{ cm}^{-1}$) lie the frequencies of the valency vibrations of C-H (of CH_2 and CH_3 groups). It should be noted that in the spectra of organosilicon compounds the number of these frequencies is considerably smaller than in the spectra of their hydrocarbon analogs (see Table 2) and corresponds to the number of frequencies to be expected from the results of calculation [13]. According to these calculated results, the group CH_3 should have two valency frequencies: symmetrical 2902 cm^{-1} and degenerate 2983 cm^{-1} . The group CH_2 should also have two frequencies: symmetrical 2884 cm^{-1} and antisymmetrical 2922 cm^{-1} .

Actually, in the spectra of trimethylsilane and tetramethylsilane we observed in each case two frequencies: about 2900 and 2960 cm^{-1} . The frequency of about 2900 cm^{-1} is evidently that of the symmetrical vibration of the group CH_3 , and the frequency of about 2960 cm^{-1} must evidently be assigned to the degenerate vibration of the group CH_3 .

Two frequencies, due to the methyl group, were observed also in the spectra of ethyltrimethylsilane, diethyldimethylsilane, and triethylmethylsilane: about 2900 cm^{-1} and about 2960 cm^{-1} . A frequency of 2880 cm^{-1} , evidently the frequency of the symmetrical vibration of the CH_2 group, was observed also. The antisymmetrical frequency of the CH_2 group did not appear, and only in the case of diethyldimethylsilane did we find a faint line at 2944 cm^{-1} , which could be assigned, evidently, to the antisymmetrical vibration of the CH_2 group. A frequency of 2735 cm^{-1} appeared in the spectra of compounds containing several ethyl groups.

The frequency 2118 cm^{-1} in the spectrum of trimethylsilane is the frequency of the valency vibration of Si-H. In comparison with the frequency of the analogous vibration in silane SiH_4 (2180 cm^{-1}), this frequency is displaced by 60 cm^{-1} .

According to Kohlrausch's interpretation [10], the frequency of 590 cm^{-1} in the spectrum of tetramethylsilane is the frequency of the fully symmetrical vibration of Si-C. In the spectra of the substances that we investigated, this frequency (region $550-600\text{ cm}^{-1}$), in passing from tetramethylsilane to tetraethylsilane, undergoes a characteristic displacement: as methyl groups are successively replaced by ethyl groups, this frequency alters in value by jumps of about 10 cm^{-1} (this frequency is marked by an asterisk in Table 1). In the spectrum of trimethylsilane this frequency has the value 623 cm^{-1} . In conclusion, we draw attention to the fact that in the spectrum of tetramethylsilane we observed two frequencies, 1249 and 1260 cm^{-1} instead of one, 1264 cm^{-1} , observed by Rank and Bordiner [8].

SUMMARY

1. The Raman spectra of the following compounds have been investigated: trimethylsilane, tetramethylsilane, ethyltrimethylsilane, diethyldimethylsilane, and triethylmethylsilane.
2. The frequencies of valency and deformation vibrations of the groups CH_2 and CH_3 lie in the same region of the spectrum as in the case of their hydrocarbon analogs.
3. The number of frequencies associated with the valency vibrations of the C-H group of CH_2 and CH_3 in the spectra of the sila-hydrocarbons investigated is less than in the spectra of their hydrocarbon analogs and corresponds to the number of frequencies to be expected from calculation data.
4. The frequency of the fully symmetrical vibration of Si-C diminishes as methyl groups are replaced by ethyl groups in the compounds investigated.

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USE OF THE SALT $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ IN THE DOUBLE-DIAZONIUM-SALT METHOD

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In the double-diazonium-salt method for the synthesis of organoantimony compounds, which was developed by one of us in conjunction with Kozheshkov [1], the initial diazonium compounds were May's salts $ArN_2Cl \cdot SbCl_3$ (Ar being phenyl, p-tolyl, o-, m-, or p-chlorophenyl, p-bromophenyl, p-iodophenyl, o- or p-anisyl, or p-phenetyl), which, when decomposed with zinc dust in boiling ethyl acetate, yield, as a rule, several products. The predominating reaction is the formation of a monoaryl derivative of trivalent antimony; formation of diarylstibinous chloride and triarylstibine dichloride proceeds to an appreciable extent, and triarylstibine is formed in insignificant amount.

Rentov and Pitsyna [2] have since shown that formation of triarylstibine dichloride in the double-diazonium salt method is a secondary reaction, which can be avoided by working up the reaction products in absence of air or at room temperature. Under these conditions only mono- and di-aryl derivatives of trivalent antimony are formed. The same authors have found also that, if after decomposition of May's salt under the usual conditions of the diazo method a further amount of May's salt is added to the reaction mixture, then the sole reaction product is a derivative of quinquevalent antimony — diphenylstibinic acid (after hydrolysis)**.

It was natural to expect that the decomposition of a double diazonium salt differing in composition from May's salt, namely one in which there are two molecules of arene-diazonium salt per molecule of antimony trichloride, i.e. $(ArN_2Cl)_2 \cdot SbCl_3$, would favor the formation of polyaryl antimony derivatives as main products of the reaction. When attempts were made to obtain a salt of this composition by reaction of two moles of benzene-diazonium chloride, prepared by diazotizing aniline in a solution of hydrochloric acid, with one molecule of antimony trichloride, only May's salt was obtained. A double diazonium salt of the composition $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ was obtained in 80% yield by diazotizing two moles of aniline hydrochloride in a methanolic solution of amyl nitrite and pouring the diazo solution obtained into a methanolic solution of antimony trichloride (one mole).

When this salt was decomposed under the conditions used for the preparation of organoantimony compounds, by the diazo method [1] (zinc in boiling ethyl acetate), the predominant reaction product was diphenylstibinous chloride (46% yield), which was accompanied by a very small amount of phenylstibinous dichloride. Decomposition of the salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ with zinc and ethanol, like that of May's salt with zinc in this solvent, gives a mixture of products, the principal one being a derivative of quinquevalent antimony — triphenylstibine dichloride. Decomposition of this salt in other solvents (acetone, benzene, chloroform, amyl acetate, diisopentyl ether, methyl formate, methanol) and in ethyl acetate with metals other than zinc (powders: antimony, copper, iron, magnesium, aluminum; aluminum and zinc amalgams and zinc-copper alloy) reduces the yield of diphenylstibinous chloride at the expense of a monophenyl derivative of trivalent antimony and triphenylstibine dichloride (Tables 1 and 2).

It was found also that, if in the synthesis of organoantimony compounds the stage involving isolation of the double diazonium salt is cut out by carrying out the diazotization of aniline hydrochloride in presence of antimony trichloride and a small amount of hydrochloric acid by means of sodium nitrite in ethyl acetate and decomposing the reaction mixture obtained with zinc, then the sole reaction product is triphenylstibine, obtained in 50-54% yield; this constitutes a new method for the preparation of this compound via a diazo compound. Triphenylstibine is the sole reaction product also when the decomposition is brought about under these conditions in presence of sodium sulfate as dehydrating agent. When decomposition is effected in presence of calcium chloride, triphenylstibine formation is supplanted by formation of triphenylstibine dichloride, which is obtained in 46% yield.

EXPERIMENTAL

Preparation of the Double Diazonium Salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$. Aniline hydrochloride (52 g, 0.4 mole) was dissolved in methanol (200 ml) and, under cooling to -5° and mechanical stirring, was diazotized with amyl nitrite (52 g — a small excess) at such a rate that the temperature did not rise above -2° . Ten to fifteen

* Deceased.

** The present work was carried out without taking the results of Rentov and Pitsyna into account.

TABLE 1

Decomposition of the Double Salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ in Various Solvents*

Solvent (50 ml)	Initial temp. (°C)	Yield on phenyl (%)			Utilization of phenyl (%)	Notes
		R_1SbCl_2	$RSbO$	R_2SbAc		
Ethanol	40-50	15.2	6.4	3.7	25.3	Very vigorous decomposition
Acetone	50	6	1.6	13.2	20.5	Ditto
Benzene	70	Traces				Very feeble decomp., not complete even after several hours
Chloroform	60	6	0.8	5.1	11.9	Very feeble decomp., heat reqd., salt not wholly decd. after several hrs.
Amyl acetate	130	2.4	2.4	17.2	22.0	Very vigorous decomposition
Diisopentyl ether	100	—	3.2	Traces	3.2	Vigorous decomposition
Methanol	60	—	1.2	13	14.2	Vigorous decomposition
Methyl formate	10.5	—	10	12.5	22.5	Ditto
Water	75	Traces	—	—	—	About 20% phenol obtained.
Liquid ammonia	Cooled with solid CO_2 and ether	—	—	—	—	Very vigorous decomposition

* For the decomposition, 15 g of double salt and 7 g Zn were taken.

minutes after addition of amyl nitrite was complete, a solution of antimony trichloride (45.6 g, 0.2 mole) in methanol (60 ml) was added. The precipitated double salt was filtered off under suction, washed twice with a small amount of methanol, twice with ether, and then dried in the air. The yield was 82-87 g).

The double diazonium salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ is a yellow powder, only slightly soluble in alcohol and acetone, decomposed by water, slightly soluble in ethyl acetate, insoluble in ether and chloroform. It decomposes at about 100°. It is stable to percussion and to temperatures of up to 40°.

Found %: N 10.18; 10.02; Sb 24.24; 23.33

 $(C_6H_5N_2Cl)_2 \cdot SbCl_3$. Calculated %: N 10.99; Sb 23.91 $C_6H_5N_2Cl \cdot SbCl_3$. Calculated %: N 7.59; Sb 33.04

Preparation of Diphenylstibinous Chloride. The decomposition of the double diazonium salt was carried out in a special vessel consisting of a 1-1.5-liter three-necked round-bottomed flask having at the bottom a cylindrical constriction (1/12-1/14 of the total volume of the flask) in which the whole of the reaction mixture was placed. The upper part of the flask was intended for the froth formed during decomposition. The flask was fitted with a Witt stirrer, the widened part of which corresponded to the lower part of the flask. The use of a vessel of this form permitted the reaction mixture to be cooled as quickly as possible at the end of the first, violent stage of the decomposition by immersing the constricted part in ice water, and it also ensured thorough stirring of the reaction mixture important to the yield. The salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ (15 g) and ethyl acetate (50 ml) were introduced into the constricted part of the flask and the mixture was stirred while zinc dust (7 g, i.e. double the theoretical amount) was poured in. Vigorous decomposition with copious frothing occurred, and the temperature rose to 75-78°. When the froth began to subside, the vessel was cooled externally with iced water, correctly timed cooling being very important; it must not be too early, or the final stage of decomposition will be affected. The whole decomposition was complete in a few seconds. When the mixture had cooled, it was filtered from the excess of zinc, and the greater part of the ethyl acetate was driven from the filtrate at somewhat reduced pressure. The solution was diluted with five times its bulk of ethanol or methanol and was poured into aqueous ammonia and ice (50 ml 25% NH_4OH , 100 ml water, 100 g ice). A sticky precipitate came down and was given several hours to settle. The greater part of the liquid was poured off, the precipitate was filtered off, and diphenylstibinous chloride was extracted from it by washing with chloroform or dichloroethane. The chloroform was driven off on a water bath, the remaining oil (diphenylstibinous chloride) was treated with a small amount of concentrated hydrochloric acid in presence of alcohol, and the precipitate was filtered off and dried; yield 42-46%. Melting point after two crystallizations from chloroform, 67-68°.

TABLE 2

Decomposition of the Double Salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ by Various Metals*

Initial temp. (°C)	Metal	Character of decomp.	Yield (%)			Utilization of C_6H_5 (%)	Notes
			R_2SbCl_3	RSbO	R_2SbAc		
75	Fe	Vigorous	—	11	Traces	11	At lower temp. decomp. is feeble
75	Sb	Moderate	12	28	3	43	It is necessary to warm to initiate decomp.
70	Cu	Moderate	Traces	12	Traces	12	Part of salt did not decompose, in spite of warming
65	Mg	Vigorous, after warming	—	2.8	7.0	9.8	
70	Al	Feeble: warming necessary during decomp.	—	8.8	—	8.8	
70	Al/Hg**	Decomp. feeble for 40 min., then more vigorous	—	8.8	—	8.8	Was warmed slightly during decomp.
70	Zn/Cu**	Very vigorous	7.2	4	14.2	25.4	
70	Zn/Hg**	Vigorous	—	5.6	10.0	15.6	

* For the decomposition, 15 g of double salt and double the theoretical amount of metal were taken; solvent: 50 ml of ethyl acetate.

** The couples Al/Hg, Zn/Hg, Zn/Cu—amalgamated Al and Zn, coppered Zn.

Preparation of Triphenylstibine. Sodium nitrite (3.7 g) was added with stirring to a cooled (+5—+10°) mixture of aniline (4.65 g), antimony trichloride (5.75 g), ethyl acetate (45 ml), and concentrated hydrochloric acid (10 ml). When addition of nitrite was complete, the reaction mixture was set aside for 40-45 minutes to enable reaction to proceed to completion. Zinc dust (6.5 g) was then added with stirring to the reaction mixture, which, owing to the fact that it contained water, was viscous. Decomposition set in immediately and proceeded very quickly without much foaming, so that the whole operation could be carried out in an ordinary beaker. When decomposition was complete, the reaction mixture was rapidly cooled externally with ice and then filtered from the zinc. The filtrate was placed in a Wurtz flask, and ethyl acetate was driven off under somewhat reduced pressure until the volume of the reaction mixture was reduced to 20 ml. It was then treated twice with 5N HCl (20 and 10 ml), and the acid aqueous layer was separated. The ethyl acetate solution was poured into a mixture of aqueous ammonia and ice (42 ml 25% NH_4OH , 25 ml water, 130 g ice). The precipitated yellowish oil, after being allowed to stand overnight, was separated from the completely clear aqueous layer and extracted with chloroform. Under these conditions dissolution was almost complete, which in itself showed that practically no phenylstibinous dichloride was formed. When solvent had been removed, the oil that remained was converted by treatment with acetic acid into pale-yellow crystals (yield of triphenylstibine, 50%). After crystallization from petroleum ether, the melting point, and the mixed melting point with authentic triphenylstibine, was 52°.

Preparation of Triphenylstibine Dichloride. The procedure was the same as in the preceding experiment on the preparation of triphenylstibine. After completion of diazotization, calcium chloride (20 g) was added, and the reaction mixture was stirred for 1-2 hours and then decomposed. The usual treatment yielded triphenylstibine dichloride (3.25 g, 46.2%), m.p. 139-142°. At the same time a small amount of a diphenylated trivalent antimony compound was formed: it was isolated as diphenylstibinous acetate (acetyldiphenylstibine) (0.7 g).

SUMMARY

1. A double diazonium salt of the composition $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ has been prepared.

2. When this salt is decomposed with zinc and ethyl acetate, diphenylstibinous chloride is formed in 42-46% yield.

3. When $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ is decomposed with zinc in acetone, methanol, methyl formate, benzene, chloroform, amyl acetate, or diisopentyl ether, or is decomposed in ethyl acetate with the following metals in powder form: copper, iron, antimony, aluminum, or magnesium, with the amalgam of aluminum or zinc, or with an alloy of zinc and copper, phenylstibinous dichloride and triphenylstibine dichloride are formed, as well as diphenylated antimony compounds. Triphenylstibine dichloride is the main reaction product in the decomposition of both the salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ and also May's salt with zinc in ethanol.

4. A method has been found for the preparation by the diazo method of triphenylstibine, which is formed in 50% yield by the decomposition with zinc of the reaction mixture containing the double diazonium salt $(C_6H_5N_2Cl)_2 \cdot SbCl_3$ obtained by diazotizing aniline with sodium nitrite in ethyl acetate in presence of antimony trichloride and hydrochloric acid.

5. When this decomposition reaction is carried out in presence of calcium chloride, triphenylstibine dichloride is obtained in 46% yield.

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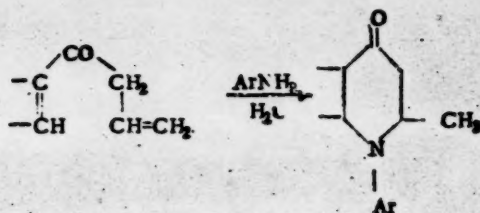
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ACETYLENE DERIVATIVES

COMMUNICATION 148. HETEROCYCLIC COMPOUNDS XXV. SYNTHESIS OF SECONDARY AND TERTIARY 2,5-DIMETHYL-1-PHENYL-4-PIPERIDINOLS AND THEIR ESTERS*

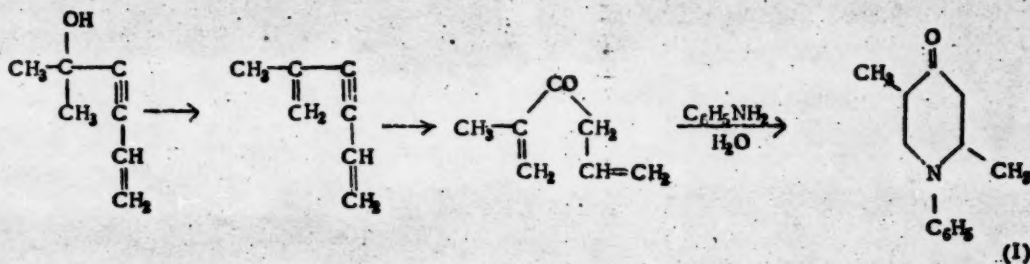
I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko

In one of our previous communications we have described a simple method for the preparation of various 1-aryl-4-piperidones: cyclization of allyl vinyl ketones by reaction with primary aromatic amines in presence of water [1]:



1-Aryl-4-piperidones have thus become quite accessible and may now be used widely in syntheses of related compounds of the piperidine series. We considered that it would be of interest to examine the effect of the aromatic residue at the nitrogen on the physiological activity of esters of 4-piperidinols.

In this paper we describe the synthesis of secondary and tertiary 2,5-dimethyl-1-phenyl-4-piperidinols and of a number of their esters. The starting material for these syntheses was 2,5-dimethyl-1-phenyl-4-piperidone (I), which is readily prepared from commercially available ethynyldimethylvinylmethanol and aniline, following the following scheme:

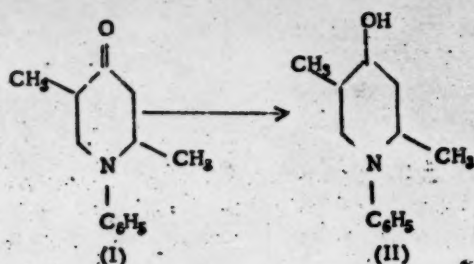


When 2,5-dimethyl-1-phenyl-4-piperidone (I) was reduced with sodium in moist ether or sodium in absolute alcohol, or was hydrogenated in presence of a platinum or nickel catalyst, a mixture of the stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidinols (II) was formed in good yield; it was separated by crystallization from benzene into α - and β -forms, melting respectively at 75-76° and 81-82°.

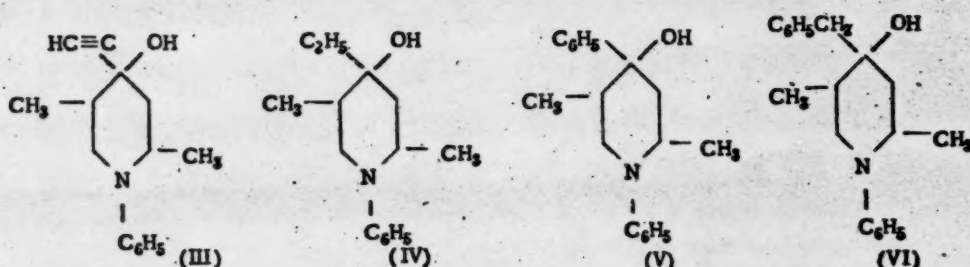
When the hydrochloride of the piperidone (I) was hydrogenated in presence of a platinum catalyst under normal conditions, only one 2,5-dimethyl-1-phenyl-4-piperidinol hydrochloride (m.p. 266-267°) was obtained; it corresponded to the low-melting base (m.p. 75-76°): (see benzene rings top of next page).

In presence of powdered caustic potash, 2,5-dimethyl-1-phenyl-4-piperidone (I) dissolved in dry ether was found to condense with acetylene, forming 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III) in 50% yield. The latter was converted by exhaustive hydrogenation of the acetylenic linkage in presence of a platinum

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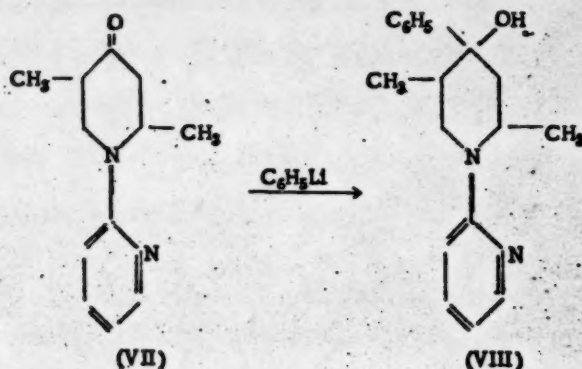
catalyst into 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) (m.p. 60-61°; hydrochloride, m.p. 205-206°). By the action of ethylmagnesium bromide on the piperidone(I) the second stereoisomer of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) was obtained in 45% yield as a liquid (hydrochloride, m.p. 186-187°):



By the action of phenyllithium on 2,5-dimethyl-1-phenyl-4-piperidone (I), 2,5-dimethyl-1,4-diphenyl-4-piperidinol (V) was formed in 83% yield; it was isolated in only one stereoisomeric form. 4-Benzyl-2,5-dimethyl-1-phenyl-4-piperidinol (VI) was prepared, also only in one stereoisomeric form, in 74% yield by the Grignard reaction, i.e. by the action of benzylmagnesium chloride on the piperidone(I).

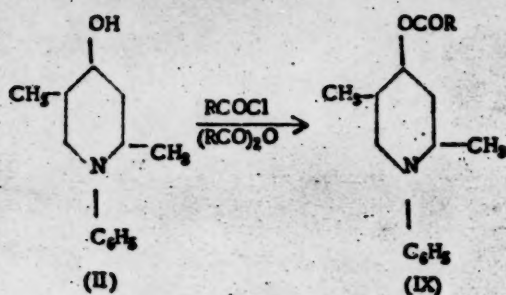
Thus, all the above-described reactions of 2,5-dimethyl-1-phenyl-4-piperidone (I) (catalytic hydrogenation of the hydrochloride, condensation with acetylene, reaction with phenyllithium and benzylmagnesium chloride) proceed in a sterically selective fashion, and in each case lead to the formation of only one stereoisomer. This behavior of 2,5-dimethyl-1-phenyl-4-piperidone is in marked contrast with that of 1-alkyl-2,5-dimethyl-4-piperidones, which always give mixtures of two or three stereoisomers in similar reactions.

By the action of phenyllithium on 2,5-dimethyl-1-(2-pyridyl)-4-piperidone (VII) [1], 2,5-dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol (VIII) is obtained in high yield; this also is isolated in only one stereoisomeric form:

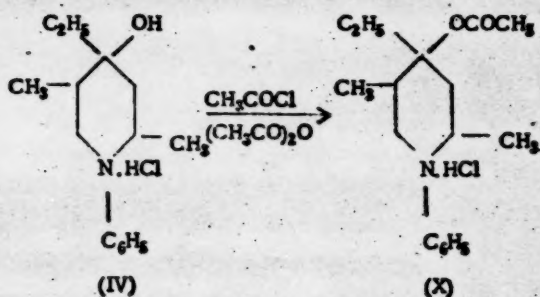


This reaction, like that of 2,5-dimethyl-1-phenyl-4-piperidone, has therefore also a sterically selective character.

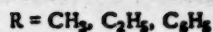
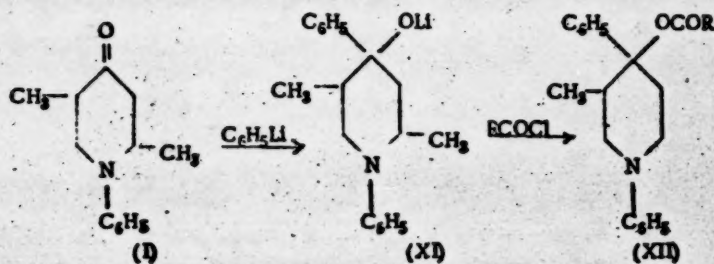
By the esterification of the two stereoisomers of 2,5-dimethyl-1-phenyl-4-piperidinol (II) with anhydrides or acid chlorides of acetic, propionic, benzoic, and p-nitrobenzoic acids, the corresponding esters were obtained. The p-nitrobenzoate was catalytically reduced in presence of platinum to the p-aminobenzoate. The esterification of the high-melting form of 2,5-dimethyl-1-phenyl-4-piperidinol was carried out by Spassow's method [2] in benzene solution in presence of magnesium turnings.



The hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV), prepared by the Grignard reaction, was acetylated with a mixture of acetyl chloride and acetic anhydride in presence of magnesium. The hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol acetic ester (X) separated directly after the reaction in the form of long rods (25-30 mm):



The esters (acetate, propionate, and benzoate) of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XII) were obtained by the action of the acid chlorides or anhydrides of the corresponding acids on the O-lithium derivative of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XI), which was obtained by the action of phenyllithium on 2,5-dimethyl-1-phenyl-4-piperidone (I):



All the esters of secondary and tertiary 1-phenyl-4-piperidinols that we prepared were converted for pharmacological tests into the hydrochlorides by saturation of their ether solutions with dry hydrogen chloride. The hydrochlorides of these esters are colorless crystalline substances, soluble, in various degrees, in water. The esters described in this paper were without anesthetic action, with the exception of the esters (IX) (α -form, $\text{R} = \text{CH}_3$) and (X), which were approximately equivalent to novacaine in anesthetic activity, but had an

irritating effect on the mucous membrane. The compounds (XII) ($R = C_2H_5$ and C_6H_5) were not tested, because of the insolubility of their hydrochlorides in water.

EXPERIMENTAL

Hydrogenation of 2,5-Dimethyl-1-phenyl-4-piperidone in Presence of a Platinum Catalyst

A solution of 2,5-dimethyl-1-phenyl-4-piperidone (b.p. 116-118°/1 mm; n_D^{20} 1.5521) (39 g) in absolute alcohol (80 ml) was hydrogenated in presence of a Pt catalyst prepared according to Adams. In the course of 26 hours, 4050 ml (20°, 746 mm) of hydrogen was absorbed instead of 4817 ml, as required theoretically. The catalyst was filtered off, the alcohol was driven off, and the product was vacuum-distilled. The product consisted of 30.5 g of a mixture of stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidinols (II), b.p. 115-120° at 0.5 mm, in the form of a colorless viscous liquid, which, after standing for a short time, solidified (m.p. 50-54°). The product was of good solubility in alcohol, benzene, gasoline, acetone, chloroform, methanol, but was insoluble in water. After being dissolved in petroleum ether (b.p. 40-60°) and then cooled to -25°, the product separated as a gelatinlike mass, which was converted, on being dried, into a powder, m.p. 69-72°.

Found %: C 76.46; 76.59; H 9.53; 9.42

$C_{13}H_{19}ON$. Calculated %: C 76.14; H 9.33

Dry hydrogen chloride was passed through an ether solution containing 25 g of the mixture of isomeric 2,5-dimethyl-1-phenyl-4-piperidinols (m.p. 50-54°). The hydrochloride that separated (18.2 g) melted after being recrystallized twice from 95% alcohol at 266-267°.

Found %: N 5.86; 5.79

$C_{13}H_{20}ONCl$. Calculated %: N 5.79

The hydrochloride of m.p. 266-267° (18 g) was dissolved in water, and the free base was precipitated with 25% aqueous ammonia and extracted with ether. The ether extract was dried over sodium sulfate. Fractionation of the ether solution yielded 14.1 g of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II), m.p. 75-76° (from petroleum ether).

Found %: N 6.99; 7.24

$C_{13}H_{19}ON$. Calculated %: N 6.82

The picrate of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol melted at 177-178.5° (from alcohol).

Found %: N 13.10; 12.90

$C_{13}H_{22}O_8N_4$. Calculated %: N 12.90

Hydrogenation of the Hydrochloride of 2,5-Dimethyl-1-phenyl-4-piperidone (I) in Presence of a Pt Catalyst

2,5-Dimethyl-1-phenyl-4-piperidone hydrochloride (m.p. 157-158°) (4.35 g) dissolved in alcohol (50 ml) was hydrogenated in presence of an Adams Pt catalyst. In the course of 18 hours, 370 ml (757 mm, 19°) of hydrogen was absorbed, against 390 ml calculated. The catalyst was filtered off. When the solvent had been distilled off, colorless crystals came down; they were recrystallized from alcohol. The product consisted of 3.8 g of the above-described hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II); it melted at 266-267°, alone and in admixture with the previous sample.

Reduction of 2,5-Dimethyl-1-phenyl-4-piperidone (I) with Sodium in Moist Ether

A mixture of 2,5-dimethyl-1-phenyl-4-piperidone (m.p. 117-118° at 1 mm; n_D^{20} 1.5522) (58 g), water (120 ml), and ether (500 ml) was introduced into a three-necked flask fitted with mercury-sealed stirrer and condenser. Sodium (67 g) in the form of small pieces was introduced into the flask under continuous stirring in such a way as to maintain the ether at a steady boil. When the whole of the sodium had been dissolved, water (100 ml) was added to the reaction mixture under vigorous stirring. The ether layer was separated and dried with sodium sulfate. Fractionation of the ether solution yielded 50.1 g of a mixture of the stereoisomers of 2,5-dimethyl-1-phenyl-4-piperidinol (II), m.p. 122-130° at 0.8 mm, in the form of a very viscous, colorless liquid, which crystallized after standing for a short time. A mixture of the product

(50 g, m.p. 50-75°) with gasoline (120 ml, b.p. 60-90°) was heated to the boil. When the solution was cooled, colorless crystals separated. A yield of 24 g of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II), m.p. 81-82° (from gasoline) was obtained.

Found %: C 75.90; 76.14; H 9.58; 9.48
 $C_{13}H_{19}ON$. Calculated %: C 76.14; H 9.33

A mixed test with the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (b.p. 75-76°) melted at 47-64°.

The hydrochloride of the high-melting 2,5-dimethyl-1-phenyl-4-piperidinol was prepared by passage of dry hydrogen chloride through an ether solution of the base (m.p. 81-82°). The sticky precipitate obtained was gradually converted into a white powder, m.p. 170-171° (from absolute alcohol), by boiling it with dry acetone.

Found %: N 6.04; 6.17
 $C_{13}H_{20}ONCl$. Calculated %: N 5.79

The high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol did not give a picrate.

The gasoline mother liquor, after separation of the high-melting isomer of the piperidinol (II) was diluted with absolute ether and saturated with dry hydrogen chloride. The hydrochloride that separated was recrystallized from 95% alcohol. The product was the hydrochloride (24.8 g) of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II) having m.p. 265-267°, and it gave no depression with the above-described sample.

Hydrogenation of 2,5-Dimethyl-1-phenyl-4-piperidone (I) Hydrochloride in Presence of Raney Nickel

2,5-Dimethyl-1-phenyl-4-piperidone hydrochloride (23 g, m.p. 157-158°) in alcohol (100 ml) was hydrogenated in a rotating 156 ml autoclave in presence of Raney nickel, the initial pressure of hydrogen being 80 atm. Hydrogenation began at 100-120° and was complete in 3 hours 30 minutes. The catalyst was filtered off, the alcohol was driven off, and the residue was treated with a 50% solution of caustic alkali. The free base that separated was extracted with ether, dried with sodium sulfate, and vacuum-distilled. The product was a non-crystallizing mixture of the stereoisomers of 2,5-dimethyl-1-phenyl-4-piperidinol (16 g) in the form of a very viscous liquid, m.p. 105-110° at 0.2 mm.

By the action of dry hydrogen chloride on an ether solution of the base and recrystallization of the salt obtained from alcohol, the hydrochloride (10 g) of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II) of m.p. 266-267° was obtained. In a mixed test with the above-described preparation, there was no depression in melting point.

Reduction of 2,5-Dimethyl-1-phenyl-4-piperidone with Sodium in Absolute Alcohol

Sodium (24 g) was added in small pieces to a solution of 2,5-dimethyl-1-phenyl-4-piperidone (m.p. 116-118° at 1 mm) (15 g) in absolute alcohol (300 ml). When the sodium had dissolved to give the ethoxide, water (100 ml) was added, and concentrated hydrochloric acid (145 ml) was added slowly with stirring until the reaction was acid. The solution of salts obtained after driving off the alcohol was evaporated in a dish on a water bath and was then filtered while hot from sodium chloride. The filtrate (about 150 ml) was saturated with alkali and extracted three times with ether. The ether solution was dried with sodium sulfate, and the residue remaining after removal of the ether was vacuum-distilled, yielding a mixture (11 g) of isomeric 2,5-dimethyl-1-phenyl-4-piperidinols, m.p. 120-126° at 1 mm, in the form of a very viscous liquid, which partially crystallized out after long standing.

The mixture of isomers was boiled with gasoline and, from the cooled solution, 6.5 g of the high-melting isomer of II, m.p. 81-82°, separated; then, by saturation of the mother liquor with dry hydrogen chloride and crystallization of the salt formed from alcohol, the hydrochloride (2.4 g; m.p. 266-267°) of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (II) was isolated.

4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III)

Dry powdered caustic potash (18 g) and dry ether (240 ml) were introduced into a three-necked flask fitted with mercury-sealed stirrer, reflux condenser, tube for the passage of acetylene, and a thermometer. The ether, which was cooled with a mixture of ice and salt (-12°), was saturated with acetylene in the course of an hour, and then, under stirring and simultaneous passage of acetylene, 2,5-dimethyl-1-phenyl-4-piperidone

(m.p. 116-118° at 1 mm; n_D^{20} 1.5520) (32 g) dissolved in ether (50 ml) was added over a period of one hour. When the ketone had been added, stirring was continued, with cooling with ice water and simultaneous passage of acetylene, for a further three hours. Passage of acetylene was then discontinued, and stirring of the reaction mixture was continued for a further hour at room temperature.

The product was treated with water (80 ml), the ether layer was separated, and the aqueous layer was saturated with solid caustic potash and carefully extracted with ether. The ether extracts were dried over sodium sulfate, and the residue remaining after removal of ether was vacuum-distilled, yielding a substance of b.p. 120-125° at 0.8 mm in the form of a very viscous liquid (25 g). This was converted by fractional precipitation into the hydrochloride. After recrystallization from absolute alcohol, 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol hydrochloride (21 g), m.p. 216.5-217.5°, was obtained.

Found %: N 5.53; 5.27

$C_{15}H_{20}ONCl$. Calculated %: N 5.26

By the action of aqueous ammonia on the pure hydrochloride (m.p. 216.5-217.5°), the free base 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III), m.p. 56-57° (from petroleum ether), was prepared.

Found %: N 6.17; 6.44

$C_{15}H_{19}ON$. Calculated %: N 6.10

4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol gave a characteristic precipitate with ammoniacal silver nitrate solution.

4-Ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV)

a) 4-Ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III) (m.p. 56-57°) (1 g) was dissolved in absolute alcohol (10 ml) and exhaustively hydrogenated in presence of an Adams platinum catalyst. In the course of one hour 215 ml of hydrogen (747 mm, 22°) was absorbed instead of 221 ml, as required by theory.

The catalyst was filtered off. The alcohol was distilled off, and the residue was dissolved by heat in gasoline; the solution, on being cooled, yielded colorless crystals, which were recrystallized from gasoline, yielding 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) (0.8 g), m.p. 60-61°, as colorless crystals in the form of long rods.

Found %: N 6.15; 6.31

$C_{15}H_{23}ON$. Calculated %: N 5.99

The hydrochloride of this isomer of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol melted at 205-206° (from alcohol).

Found %: N 5.27; 5.22

$C_{15}H_{24}ONCl$. Calculated %: N 5.19

A solution of 2,5-dimethyl-1-phenyl-4-piperidone (10 g) in absolute ether (15 ml) was added dropwise to a solution, cooled with ice and salt, of ethylmagnesium bromide, which was prepared from magnesium turnings (1.2 g), ethyl bromide (6 g), and absolute ether (26 ml). When addition of the piperidone was complete, stirring was continued for one hour at room temperature and for a further two hours at the boiling point of ether. The reaction mixture was treated with 18% hydrochloric acid (30 ml). The ether layer was separated, and the aqueous layer was saturated with caustic potash and extracted with ether. The ether extract was dried over magnesium sulfate, and the residue remaining after removal of ether was vacuum-distilled, yielding 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV) (8 g) as a very viscous colorless liquid, b.p. 110-112°/0.3 mm. The ether solution of the base was saturated with hydrogen chloride, and the salt that separated was recrystallized from a mixture of alcohol and ethyl methyl ketone, yielding 6 g of the hydrochloride of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 186-187°, in the form of fine glistening crystals, which were soluble in water.

Found %: N 5.27; 5.16

$C_{15}H_{24}ONCl$. Calculated %: N 5.19

4-Benzyl-2,5-dimethyl-1-phenyl-4-piperidinol (VI)

A solution of 2,5-dimethyl-1-phenyl-4-piperidone (I) (20 g) in absolute ether (30 ml) was added dropwise to a solution, cooled with ice water, of benzylmagnesium chloride, which was prepared from magnesium turnings

(2.4 g), benzyl chloride (12.7 g), and absolute ether (50 ml). When addition of the piperidone was complete, stirring was continued for 40 minutes at room temperature and then for one hour at the boiling point of ether. The reaction product was decomposed with 18% hydrochloric acid (60 ml) and the precipitated oily material was separated and treated with acetone. The crystals of hydrochloride that separated were recrystallized from alcohol, yielding 24 g of the hydrochloride of 4-benzyl-2,5-dimethyl-1-phenyl-4-piperidinol (VI) as colorless crystals, insoluble in water, m.p. 222-224°.

Found %: N 4.20; 4.45

$C_{20}H_{26}ONCl$. Calculated %: N 4.22

2,5-Dimethyl-1,4-diphenyl-4-piperidinol (V)

The whole experiment was carried out in a stream of nitrogen. Absolute ether (40 ml) and fine lithium turnings (1.6 g) were introduced into a three-necked flask fitted with stirrer, reflux condenser, dropping funnel, thermometer, and a tube for the passage of nitrogen. Bromobenzene (1.5 g) was added to the mixture, and when the reaction had set in a further 16 g of bromobenzene, dissolved in absolute ether (50 ml), was added gradually. Absolute ether (150 ml) was then added to the mixture, and the reaction mixture was heated for two hours at the boiling point of ether.

When reaction was complete, the flask containing the phenyllithium was cooled to -12°, and a solution of 2,5-dimethyl-1-phenyl-4-piperidone (15 g) in ether (20 ml) was added dropwise with stirring over a period of 50 minutes. The contents of the flask were stirred at room temperature for two hours and then at the boiling point of ether for two hours. The reaction product was acidified with 15% hydrochloric acid at 0°, when a dark-colored precipitate formed at the bottom of the flask. After separation of the ether and water layers, this precipitate was treated with acetone. The crystals of hydrochloride that were isolated were recrystallized from propyl alcohol, yielding 19.5 g of the hydrochloride of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (V), m.p. 237-238.5°.

Treatment of this hydrochloride (m.p. 237-238.5°) with 25% aqueous ammonia yielded 2,5-dimethyl-1,4-diphenyl-4-piperidinol (V), m.p. 108-108.5° (from a mixture of gasoline and ethyl methyl ketone).

Found %: H 8.43; 8.45; C 80.60; 80.40; N 5.32; 5.28

$C_{19}H_{25}ON$. Calculated %: H 8.53; C 81.04; N 4.98

The hydrobromide, obtained by saturation of an ether solution of the base with dry hydrogen bromide, melted at 238-240° (from alcohol).

Found %: N 3.97; 3.79

$C_{19}H_{24}ONBr$. Calculated %: N 3.86

The oxalate, obtained by the mixing of solutions of the base and of anhydrous oxalic acid in absolute ether, melted at 218-220° (from 50% alcohol).

Found %: N 4.11; 4.26

$(C_{19}H_{25}ON)_2 \cdot (COOH)_2$. Calculated %: N 4.29.

The hydrochloride, hydrobromide, and oxalate of 2,5-dimethyl-1,4-diphenyl-4-piperidinol are insoluble in water.

2,5-Dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol (VIII)

Phenyllithium was prepared in the manner described above from lithium turnings (0.9 g), bromobenzene (11.5 g), and absolute ether (100 ml). The reaction was carried out in a stream of dry nitrogen. The flask containing the phenyllithium was cooled to -10°, and a solution of 2,5-dimethyl-1-(2-pyridyl)-4-piperidone (VII) (10 g) of m.p. 71° in absolute ether (25 ml) was added dropwise. On the next day the dark-colored reaction mixture was heated for two hours at the boiling point of ether, and was then acidified with 10% hydrochloric acid at 0°. The oily precipitate that formed was separated and dissolved in warm concentrated hydrochloric acid. Neutral substances were removed by ether extraction. The free base was separated by the action of a 50% solution of caustic potash, and was extracted with ether. A stream of dry hydrogen chloride was passed through the dry ethereal solution of the base until it was saturated. The precipitated hydrochloride was washed with acetone and recrystallized from absolute alcohol, yielding 9.5 g of the monohydrochloride of 2,5-dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol, m.p. 226.5-227.5°, in the form of glistening crystals, which were insoluble in water, but soluble in warm concentrated hydrochloric acid.

Found %: N 8.97; 9.17; Cl 11.48
 $C_{18}H_{23}ON_2Cl$. Calculated %: N 8.78; Cl 11.13

The hydrochloride (m.p. 226.5-227.5°), when treated with a solution of caustic potash, yielded the free base, 2,5-dimethyl-4-phenyl-1-(2-pyridyl)-4-piperidinol (VIII) m.p. 112.5-114° (from a mixture of gasoline and acetone).

Found %: N 10.17; 9.96
 $C_{18}H_{22}ON_2$. Calculated %: N 9.92

Benzoic Ester of the Low-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, α -form: $R = C_6H_5$)

Benzoyl chloride (15 ml) was added to 3.2 g of the hydrochloride of the low-melting 2,5-dimethyl-1-phenyl-4-piperidinol (II, α -form; m.p. 266-267°), and the mixture was heated at 130-145° for four hours. The excess of benzoyl chloride was driven off under reduced pressure, and the residue was crystallized from 50% alcohol, yielding 3 g of the water-insoluble benzoic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 217-218°.

Found %: N 4.34; 4.53
 $C_{28}H_{34}O_2NCl$. Calculated %: N 4.05

The free base of the benzoic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, $R = C_6H_5$) was obtained by shaking the hydrochloride (m.p. 217-218°) with aqueous ammonia. Large crystals, m.p. 68-70° (from gasoline), were obtained.

Found %: N 4.83; 5.08
 $C_{28}H_{33}O_2N$. Calculated %: N 4.53

Acetic Ester of the Low-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, α form: $R = CH_3$)

a) A mixture of the hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 266-267°; 5 g) and acetic anhydride (50 ml) was saturated with dry hydrogen chloride and heated on a boiling water bath for four hours. The excess of acetic anhydride was removed under reduced pressure, and the residue was recrystallized from water, yielding 4 g of the hydrochloride of the acetic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 254-255°.

Found %: N 5.10; 4.93
 $C_{15}H_{22}O_2NCl$. Calculated %: N 4.93

The free base of the acetic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, $R = CH_3$) was obtained in the usual way from the hydrochloride (m.p. 254-255°) in the form of colorless crystals, m.p. 84-85° (from gasoline).

Found %: N 5.77; 5.93
 $C_{15}H_{21}O_2N$. Calculated %: N 5.67

b) A mixture of 2.5 g of the hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 266-267°) and 25 ml of acetyl chloride was boiled on a water bath for four hours. The excess of acetyl chloride was removed, and the residue was recrystallized from water, yielding 1.8 g of the above-described hydrochloride of the acetic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol, m.p. 254-255°.

Propionic Ester of the Low-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, α -form: $R = C_2H_5$)

Propionic anhydride (10 ml) was added to a boiling mixture of 6.5 g of the hydrochloride of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 266-267°) and 35 ml of propionyl chloride until the precipitate present dissolved completely. The homogeneous reaction mixture was boiled for three hours. After removal under reduced pressure of the excess of propionyl chloride and propionic anhydride, the residue was recrystallized from ethyl methyl ketone, yielding 6.1 g of the hydrochloride of the propionic ester of the low-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, $R = C_2H_5$), m.p. 193-194°.

Found %: N 4.92; 4.77
 $C_{16}H_{24}O_2NCl$ Calculated %: N 4.70

Benzoic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol
(IX, β -form: $R = C_6H_5$)

The esterification was carried out by Spassow's method [2]. A solution of 7 g of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 81-82°) in 30 ml of dry benzene was added to a mixture of benzoyl chloride (14 ml) and magnesium turnings (1.3 g). The reaction mixture was heated on a boiling water bath for three hours, and the excess of benzoyl chloride was then driven off under reduced pressure. The residue was diluted with water, neutralized with sodium carbonate, and extracted with ether. The product, after removal of ether, was vacuum-distilled, yielding 6 g of the benzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol (high-melting form) (IX, $R = C_6H_5$), b.p. 160-165°/1 mm, which rapidly crystallized out, giving colorless crystals, m.p. 62.5-63.5° (from gasoline).

Found %: N 4.59; 4.79
 $C_{22}H_{23}O_2N$ Calculated %: N 4.53

The hydrochloride of the benzoic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol was prepared by the action of dry hydrogen chloride on an ether solution of the base; it melted at 149-151° (from a mixture of ethyl methyl ketone and absolute alcohol).

Found %: N 4.05; 4.26
 $C_{16}H_{24}O_2NCl$ Calculated %: N 4.05

On being dissolved in water, the hydrochloride was hydrolyzed with separation of the free base of the benzoic ester, (m.p. 62.5-63.5°).

Acetic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol
(IX, β -form: $R = CH_3$)

The esterification was carried out by Spassow's method [2]. A solution of 4.1 g of the high-melting form of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 81-82°) in 18 ml of dry benzene was added to a mixture of acetyl chloride (3.6 g) and magnesium turnings (0.6 g). The reaction was accompanied by evolution of heat, and the reaction mixture rapidly set into a crystalline mass. The product was diluted with water (20 ml), neutralized with sodium carbonate, and extracted with ether. The ether solution was dried with sodium sulfate, and the residue, after removal of ether, was vacuum-distilled, yielding 4.2 g of a substance of b.p. 135-138°/1 mm which was converted into its hydrochloride by saturating its ether solution with dry hydrogen chloride. The product (4.1 g) was the hydrochloride of the acetic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, $R = CH_3$), m.p. 180-181.5° (from a mixture of alcohol and ether).

Found %: N 4.97; 5.26
 $C_{15}H_{21}O_2NCl$ Calculated %: N 4.93

p-Nitrobenzoic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol
(IX, β -form: $R = C_6H_4NO_2-p$)

A solution of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 81-82°) (14 g) in dry benzene (30 ml) was added to a mixture of p-nitrobenzoyl chloride (25 g), dissolved in 25 ml of benzene, and magnesium turnings (1.8 g). The reaction mixture was heated on a boiling water bath for six hours. On the next day the reaction product was treated with 18% hydrochloric acid, and the crystalline precipitate that separated was filtered off and washed with concentrated hydrochloric acid. The crude hydrochloride was recrystallized twice from a mixture of ethyl methyl ketone and absolute alcohol, yielding 19.5 g of the hydrochloride of the p-nitrobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol (high-melting form) in the form of fine colorless crystals, m.p. 195-196°.

Found %: N 7.07; 7.35
 $C_{20}H_{23}O_4N_2Cl$ Calculated %: N 7.21

The hydrochloride was readily hydrolyzed by water with the formation of the free base of the p-nitrobenzoic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, $R = C_6H_4NO_2-p$) as a yellow powder of m.p. 130-131° (from gasoline).

Found %: N 8.16; 7.91
 $C_{20}H_{22}O_4N_2$. Calculated %: N 7.90

p-Aminobenzoic Ester of the High-melting Isomer of 2,5-Dimethyl-1-phenyl-4-piperidinol (IX, B-form: R = $C_6H_4NH_2$ -p)

The hydrochloride of the p-nitrobenzoic ester of 2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 195-196°; 11 g) was dissolved in warm 90% alcohol (130 ml) and hydrogenated in presence of a platinum catalyst prepared according to Adams. During the shaking, a part of the nitrobenzoic ester crystallized out in the flask, but as hydrogenation proceeded the whole of the precipitate went into solution. When 2120 ml (747 mm, 22°) of hydrogen had been absorbed, the catalyst was filtered off, alcohol was removed, under reduced pressure, and the residue was dissolved in water. The free base was precipitated from the aqueous solution by addition of 25% aqueous ammonia. Recrystallization from a mixture of gasoline and ethyl methyl ketone yielded 7 g of the p-aminobenzoic ester of the high-melting isomer of 2,5-dimethyl-1-phenyl-4-piperidinol (IX, R = $C_6H_4NH_2$ -p), m.p. 157-158°.

Found %: N 8.63; 8.53
 $C_{20}H_{24}O_2N_2$. Calculated %: N 8.63

Acetic Ester of 4-Ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (X)

Acetyl chloride (10 ml) was added to 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (m.p. 186-187°; 2.7 g). Acetic anhydride (3 ml) was added to the boiling reaction mixture in order to effect complete solution of the hydrochloride. The mixture was boiled on a water bath for five hours. The excess of acetyl chloride was distilled off, and the residue was crystallized from ethyl methyl ketone, yielding 2.5 g of the hydrochloride of the acetic ester of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol [the liquid stereoisomer (IV)] as long (25-30 mm) crystals, m.p. 182-183°.

Found %: N 4.77; 4.56
 $C_{17}H_{26}O_2NCl$. Calculated %: N 4.49

In admixture with the original hydrochloride of the piperidinol it melted at 153-158°.

Benzoic Ester of 2,5-Dimethyl-1,4-diphenyl-4-piperidinol (XII; R = C_6H_5)

2,5-Dimethyl-1-phenyl-piperidone (20 g) dissolved in absolute ether (30 ml) was added dropwise over a period of one hour to a solution, cooled to -10° of phenyllithium, prepared from lithium turnings (2 g), bromobenzene (20 ml), and absolute ether (150 ml). The mixture was stirred at room temperature for two hours, and then at the boiling point of ether for 1 hr 30 min. The solution of O-lithium derivative so obtained was cooled with ice water, and a solution of freshly distilled benzoyl chloride (20 g) in absolute ether (30 ml) was added. On the next day the mixture was heated for four hours at the boil. The reaction product, after being cooled, was acidified with 10% hydrochloric acid, and the precipitate that formed was washed with hot 50% alcohol.

The product (25 g) was the hydrochloride of the benzoic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (colorless crystals, insoluble in water), m.p. 187-188° (from a mixture of alcohol and benzene).

Found %: N 3.12; 3.30
 $C_{26}H_{28}O_2NCl$. Calculated %: N 3.32

Shaking of the hydrochloride (m.p. 187-188°) with 25% aqueous ammonia yielded the free base of the benzoic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XII, R = C_6H_5) in the form of glistening plates, m.p. 178-179° (from petroleum ether).

Found %: N 3.89; 4.02
 $C_{26}H_{28}O_2N$. Calculated %: N 3.64

Propionic Ester of 2,5-Dimethyl-1,4-diphenyl-4-piperidinol (XII; R = C_6H_5)

A solution of propionic anhydride (20 g) in absolute ether (30 ml) was added dropwise, under cooling with ice water and stirring, to a solution of the O-lithium derivative of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, prepared as in the previous experiment from lithium turnings (2 g), bromobenzene (20 ml) and 2,5-dimethyl-1-phenyl-4-piperidone (18.5 g) in absolute ether (210 ml). The reaction mixture became thick and yellow. On the next day the mixture was boiled for four hours, and the reaction product was hydrolyzed with dilute hydrochloric acid (1:3). The precipitated crude hydrochloride was recrystallized from a mixture of alcohol and

acetone, yielding 18 g of the hydrochloride of the propionic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, m.p. 167-168°, a substance of low solubility in water.

Found %: N 3.71; 3.80

$C_{22}H_{25}O_2NCl$ Calculated %: N 3.75

Treatment of the hydrochloride (m.p. 167-168°) with aqueous ammonia yielded the free base of the propionic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol (XII, $R = C_2H_5$) in the form of large (8-12 mm) plates of m.p. 88-90° (from gasoline).

Found %: N 4.39; 4.49

$C_{24}H_{29}O_2N$ Calculated %: N 4.15

Acetic Ester of 2,5-Dimethyl-1,4-diphenyl-4-piperidinol (XII; $R = CH_3$)

A solution of acetic anhydride (20 ml) in absolute ether (30 ml) was added dropwise, under cooling with ice water and stirring, to a solution of the O-lithium derivative of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, prepared from lithium turnings (2 g), bromobenzene (20 ml), 2,5-dimethyl-1-phenyl-4-piperidone (18 g), and absolute ether (200 ml). The further procedure was as above and yielded 16 g of the hydrochloride of the acetic ester of 2,5-dimethyl-1,4-diphenyl-4-piperidinol, m.p. 176-177.5° (from 60% alcohol), in the form of glistening needles of poor solubility in water.

Found %: N 3.76; 3.91

$C_{24}H_{27}O_4NCl$ Calculated %: N 3.89

SUMMARY

1. Reduction of 2,5-dimethyl-1-phenyl-4-piperidone (I) by sodium in moist ether, by sodium in alcohol, or by hydrogenation in presence of a platinum or nickel catalyst yields two stereoisomeric 2,5-dimethyl-1-phenyl-4-piperidols (II).
2. Hydrogenation of the hydrochloride of 2,5-dimethyl-1-phenyl-4-piperidone in presence of a platinum catalyst gives only one stereoisomeric form, which corresponds to the low-melting form of the base (II, α -form).
3. A number of tertiary 4-piperidinols have been prepared by the action of alkylmagnesium halides and of phenyllithium on 2,5-dimethyl-1-phenyl-4-piperidone (I) and on 2,5-dimethyl-1-(2-pyridyl)-4-piperidone (VII). It has been established that in each case only one stereoisomeric form of the tertiary 4-piperidinol was formed.
4. By means of the condensation of 2,5-dimethyl-1-phenyl-4-piperidone with acetylene in presence of powdered caustic potash, the preparation has been effected in 50% yield of 4-ethynyl-2,5-dimethyl-1-phenyl-4-piperidinol (III), which was converted, by exhaustive hydrogenation, in the second stereoisomer of 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol (IV).
5. The syntheses have been carried out of esters of both isomeric forms of 2,5-dimethyl-1-phenyl-4-piperidinol with acetic, propionic, benzoic, p-nitrobenzoic, and p-aminobenzoic acids.
6. By means of various methods of esterification, the esters formed by 4-ethyl-2,5-dimethyl-1-phenyl-4-piperidinol and by 2,5-dimethyl-1,4-diphenyl-4-piperidinol with acetic, propionic and benzoic acids have been prepared.

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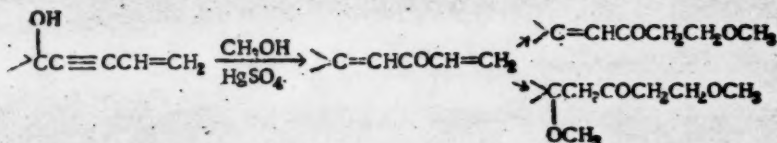
ACETYLENE DERIVATIVES

COMMUNICATION 149. SYNTHESIS OF β -AMINO KETONES BY THE ACTION OF SECONDARY AMINES ON β -METHOXY KETONES AND α,β -UNSATURATED KETONES

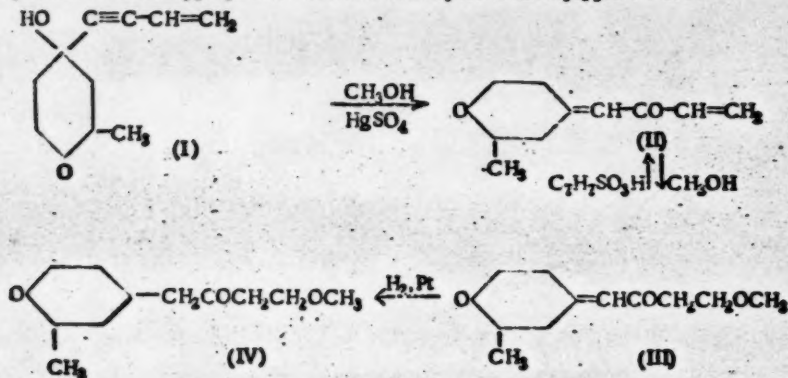
I. N. Nazarov and S. A. Vartanyan

β -Amino ketones have recently found wide application for the synthesis of various physiologically active substances [1,2], and the development, therefore, of simple methods for their preparation may be of considerable importance for the further development of work directed to the discovery of new chemico-pharmaceutical and medicinal preparations.

As we have shown in a previous paper [3], β -methoxy ketones react readily with secondary amines with formation in high yield of the corresponding β -amino ketones, which may be prepared also by the direct addition of amines to α,β -unsaturated ketones. We have found in our laboratory that (vinylethynyl)-methanols readily isomerize under the influence of mercuric sulfate in methanol solution to give divinyl ketones, which, under the conditions of the experiment, combine with one or two molecules of methanol, yielding the corresponding β -methoxy ketones [4]:

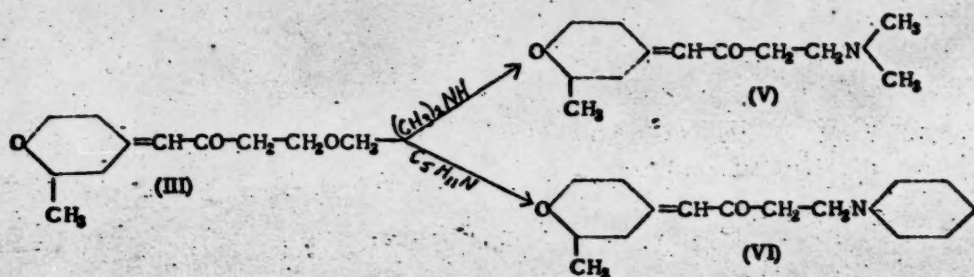


Continuing these investigations, we have now shown that tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol (I) also undergoes isomerization under the influence of mercuric sulfate in methanol solution, yielding the dienone II, which, under the conditions of the reaction, combines at the unsubstituted vinyl group with one molecule of methanol, forming the unsaturated methoxy ketone III. The free divinyl ketone (II) was prepared by vacuum distillation of the unsaturated methoxy ketone III in presence of *p*-toluenesulfonic acid [5]. The methoxy ketone III, when hydrogenated at a platinum catalyst, was converted into the saturated methoxy ketone IV. The structure of the methoxy ketone III was definitely proved by the aid of permanganate oxidation, which yielded 3-methoxypropionic acid and tetrahydro-2-methylpyran-4-one:

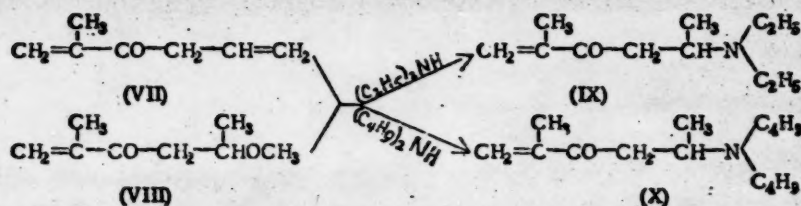


By the action of aqueous solutions of dimethylamine and of pyridine on the methoxy ketone III, the corresponding β -amino ketones V and VI were prepared: (See top of next page).

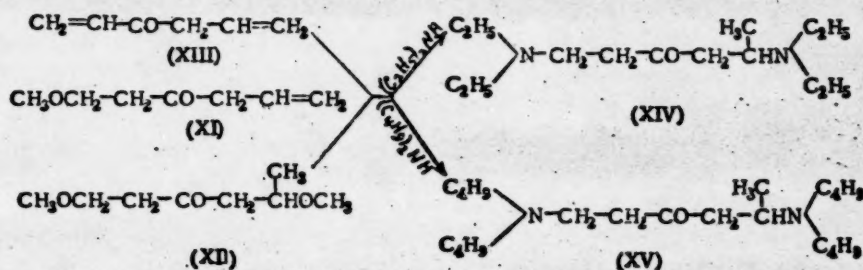
It was found that similar syntheses of amino ketones by the aid of diethyl- and dibutyl-amines did not go so smoothly and that it was better to obtain the required products by direct addition of these amines to α,β -unsaturated ketones, which are readily prepared by distillation of the corresponding β -methoxy ketones in presence of *p*-toluenesulfonic acid [5].



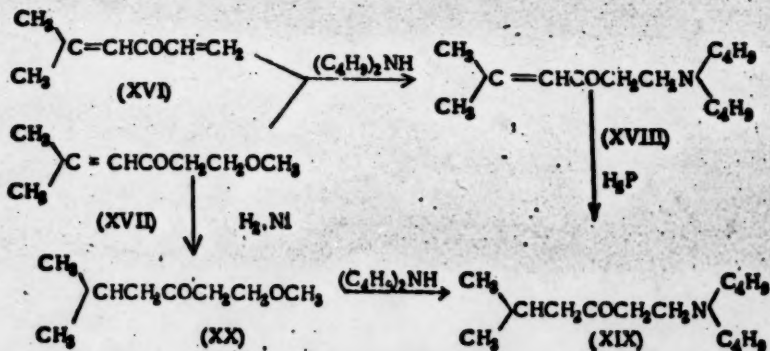
By the action of an aqueous solution of diethylamine on the methoxy ketone VIII [6], the synthesis was effected in poor yield of the amino ketone IX, which was obtained in good yield also by the direct addition of diethylamine to 2-methyl-1,5-hexadien-3-one (VII). In a similar way, the amino ketone X was prepared by the action of dibutylamine on the methoxy ketone VIII and by the direct addition of dibutylamine to the dienone VII:



The action of an aqueous solution of diethylamine on a mixture of the methoxy ketones XI and XII [7] gave 1,5-bis(diethylamino)-3-hexanone (XIV) in poor yield. The same diamino ketone was obtained in good yield by direct addition of diethylamine to 1,5-hexadien-3-one (XIII). This reaction went in a similar way when dibutylamine was used, and in this case 1,5-bis(dibutylamino)-3-hexanone (XV) was obtained:



When 5-methyl-1,4-hexadien-3-one (XVI) [5] and 1-methoxy-5-methyl-5-hexen-3-one (XVII) [4] were each treated with an aqueous solution of butylamine, the same amino ketone, 1-dibutylamino-5-methyl-4-hexen-3-one (XVIII), was obtained in each case, and when this was hydrogenated in presence of a platinum catalyst one molecule of hydrogen was absorbed with formation of 1-dibutylamino-5-methyl-3-hexanone (XIX). This amino ketone was prepared also by the action of dibutylamine on 1-methoxy-5-methyl-3-hexanone (XX) [8]:



It must be pointed out that, in the reactions of secondary amines with β -methoxy ketones, some volatile products were formed in all cases; they were not investigated. None of the amino ketones described in this paper gave a crystalline picrate: treatment with picric acid led to precipitation of a thick mass, which did not crystallize.

EXPERIMENTAL

Tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol (I) was prepared by the action of vinylacetylenemagnesium bromide on tetrahydro-2-methylpyran-4-one, as previously described [9]. Distillation of the pyranol (I) was carried out in presence of pyrogallol (b.p. 100-102° at 4 mm; n_D^{20} 1.5048).

Isomerization of Tetrahydro-2-methyl-4-(vinylethynyl)pyran-4-ol

A mixture of the pyranol (I) (150 g), distilled methanol (370 g), and finely ground mercuric sulfate (3 g) was stirred for 8.5 hr at 35-40°. During this period, more mercuric sulfate was added (10 g, making 13 g in all). The reaction mixture was poured off the catalyst, neutralized with a solution of sodium carbonate, and extracted with ether; the extract was dried over sodium sulfate, repeated vacuum fractionation yielded the methoxy ketone (III) (80 g) in the form of a mobile liquid of characteristic odor; b.p. 109-111° at 1 mm; n_D^{20} 1.4800; d_4^{20} 1.0340; found MR 54.38; calculated MR 53.64.

Found %: C 66.19; 66.39; H 9.51; 9.77

$C_{11}H_{12}O_3$. Calculated %: C 66.66; H 9.20

Hydrogenation of the Methoxy Ketone (III)

Freshly distilled methoxy ketone (III) (b.p. 109-111° at 1 mm; n_D^{20} 1.4800) (3 g) was hydrogenated in ethanolic solution in presence of a platinum catalyst. The volume of hydrogen absorbed was 350 ml instead of 363 ml required by theory. The saturated methoxy ketone (IV) (2.3 g) was obtained in the form of a colorless, odorless liquid having b.p. 90-92° at 2 mm; n_D^{20} 1.4600; d_4^{20} 0.9987; found MR 54.23; calculated MR 54.09.

Found %: C 66.30; H 10.11

$C_{11}H_{14}O_3$. Calculated %: C 66.00; H 10.00

Oxidation of the Methoxy Ketone (III)

The methoxy ketone (III) (17 g) was mixed with water (200 ml), and to this mixture finely ground potassium permanganate (31 g) was added in small portions over a period of six hours under continuous stirring. The reaction mixture was set aside overnight, and stirring was continued on the next day for a further seven hours. Manganese dioxide was filtered off and washed with hot water; the neutral products were extracted with ether, and the extract was dried over sodium sulfate and vacuum distilled, yielding tetrahydro-2-methylpyran-4-one (b.p. 51-52° at 12 mm; n_D^{20} 1.4440). (4.2 g). Its semicarbazone melted at 169-170° and did not show depression with an authentic specimen [7]. The solution of salts was evaporated to dryness, decomposed with concentrated hydrochloric acid (20 ml), and carefully extracted with ether. After drying of the extract and removal of ether, the residue was vacuum-distilled, yielding 3-methoxypropionic acid, b.p. 100-103° at 12 mm; n_D^{20} 1.4200.

Preparation of the Dienone (II)

The methoxy ketone (III) (10 g) and *p*-toluenesulfonic acid (0.1 g) were introduced into a flask fitted with a fractionating column and heated at 100-110° at a pressure of 12 mm for 30 minutes. Methanol split off and the divinyl ketone slowly distilled over. Redistillation yielded the dienone (II) (5 g) as a yellow liquid having a sharp odor; b.p. 101-104° at 4 mm; n_D^{20} 1.4919; d_4^{20} 1.0050; found MR 47.98; calculated MR 46.90.

Found %: C 72.06; 72.01; H 8.79; 8.45

$C_{10}H_{14}O_2$. Calculated %: C 72.29; H 8.43

Preparation of the Amino Ketone (V)

A mixture of the methoxy ketone (III) (b.p. 109-111° at 1 mm; n_D^{20} 1.4800) and a 20% aqueous solution (50 g) of dimethylamine was heated in an autoclave at 80° for five hours. The excess of dimethylamine was removed under reduced pressure on a water bath at 45°. The solution was rendered slightly acid with hydrochloric acid and the neutral products were extracted with ether. The extract was dried with sodium sulfate and vacuum-distilled, yielding unchanged methoxy ketone (b.p. 109-112° at 1 mm; n_D^{20} 1.4810) (8.1 g).

The organic bases were salted out with potassium carbonate and extracted with ether. The ether extract was dried with sodium sulfate and vacuum-distilled, yielding the amino-ketone (V) (6.3 g) as a thick liquid of characteristic amine odor, which yellowed on standing; b.p. 128-130° at 4 mm; n_D^{20} 1.5040; d_4^{20} 1.0370; found MR 60.30; calculated MR 59.85.

Found %: N 6.83; 6.64

$C_{12}H_{21}O_2N$. Calculated %: N 6.63

Preparation of the Amino Ketone (VI)

Piperidine (10 g) and water (3 g) were added to the methoxy ketone (III) (12 g). When the water was added the temperature rose to 45°. The mixture was heated at 80° for three hours and was then treated as in the previous experiment. The product was the amino ketone (VI), b.p. 138-140° at 4 mm; n_D^{20} 1.5150; d_4^{20} 1.0440; found MR 72.68; calculated MR 72.20.

Found %: N 5.20; 5.19

$C_{15}H_{25}O_2N$. Calculated %: N 5.57

Preparation of the Amino Ketone (IX)

a) Diethylamine (10 g) was added dropwise to 2-methyl-1,5-hexadien-3-one (VII) (b.p. 80-83° at 80 mm; n_D^{20} 1.4713) (15 g) [6]; the temperature of the mixture was found to rise to 65°. The mixture was then heated in a glass ampoule at 80° for three hours and was then treated as in the preceding experiments. The ether solution of the organic base was dried over magnesium sulfate, and the product was vacuum-distilled, yielding 5-diethylamino-2-methyl-1-hexen-3-one (IX) as a clear liquid of characteristic odor that yellowed on standing; b.p. 94-95° at 7 mm; n_D^{20} 1.4580; d_4^{20} 0.8821; found MR 56.62; calculated MR 56.40.

Found %: N 8.07

$C_{11}H_{21}ON$. Calculated %: N 7.65

b) 5-Methoxy-2-methyl-1-hexen-3-one (VIII) (b.p. 56-59° at 6 mm; n_D^{20} 1.4400) (15 g) [6], diethylamine (15 g), and water (5 g) were heated together in a glass ampoule at 60° for two hours and then treated in the usual way. The ether solution of the organic base was dried with magnesium sulfate, and the product was vacuum-distilled, yielding the above-described 5-diethylamino-2-methyl-1-hexen-3-one (IX), b.p. 109-112° at 10 mm; n_D^{20} 1.4580.

Preparation of the Amino Ketone (X)

a) Dibutylamine (11 g) was added dropwise to 2-methyl-1,5-hexadien-3-one (VII) (b.p. 80-83° at 80 mm; n_D^{20} 1.4710) (15 g); the temperature of the mixture was observed to rise to 45°. The mixture was heated at 80° for six hours and then treated in the usual way, yielding 5-dibutylamino-2-methyl-1-hexen-3-one (X); b.p. 110-112° at 3 mm; n_D^{20} 1.4620; d_4^{20} 0.8740; found MR 75.46; calculated MR 74.95.

Found %: N 6.27; 5.93

$C_{15}H_{29}ON$. Calculated %: N 5.84

b) A mixture of 5-methoxy-2-methyl-1-hexen-3-one (VIII) (b.p. 56-59° at 6 mm; n_D^{20} 1.4400) (10 g), dibutylamine (10 g) and water (2 g) was heated in a glass ampoule for three hours at 60°. The usual treatment yielded 1.3 g of the amine ketone (X), b.p. 111-113° at 2 mm; n_D^{20} 1.4620.

Preparation of the Diamino Ketone (XIV)

a) Diethylamine (16 g) was added dropwise to 1,5-hexadien-3-one (XIII) (b.p. 40-42° at 12 mm; n_D^{20} 1.4729) (10 g) [7]. The temperature of the reaction mixture rose to 65°, and the mixture was heated in a glass ampoule for three hours at 70° and was then vacuum-fractionated, yielding 1,5-bis(diethylamino)-3-hexanone (XIV) (18.5 g) as a clear liquid that yellowed on standing; b.p. 94-95° at 5 mm; n_D^{20} 1.4630; d_4^{20} 0.8924; found MR 74.68; calculated MR 74.77.

Found %: N 11.46

$C_{14}H_{30}ON_2$. Calculated %: N 11.57

b) The mixture of methoxy ketones (XI and XII) (b.p. 40-42° at 12 mm; n_D^{20} 1.4330) (10 g) [7] was heated together with diethylamine (10 g) and water (2 g) at 60° for four hours. The excess of diethylamine was driven off under reduced pressure on a water bath at 45°. The organic bases were salted out with potassium

carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding the above-described 1,5-bis(diethylamino)-3-hexanone (XIV) (1.7 g); b.p. 96-98° at 8 mm; n_D^{20} 1.4628.

Preparation of the Diamino Ketone (XV)

a) Dibutylamine (18 g) was added to 1,5-hexadien-3-one (XIII) (b.p. 40-42° at 12 mm; n_D^{20} 1.4730) (10 g), and the temperature of the reaction mixture rose to 67°. When the dibutylamine had been added, the reaction mixture was heated in a glass ampoule for one hour at 70°, and was then vacuum-fractionated, yielding 1,5-bis(dibutylamino)-3-hexanone (XV) (17.3 g) as a clear liquid, b.p. 110-111° at 1 mm; n_D^{20} 1.4620; d_4^{20} 0.8680; found MR 112.10, calculated MR 111.73.

Found %: N 8.21; 8.04

$C_{22}H_{40}ON_2$. Calculated %: N 7.91

b) A mixture of the methoxy ketones (XI) and (XII) (b.p. 85-89° at 9 mm; n_D^{20} 1.4330), (20 g) was heated with dibutylamine (20 g) and water (4 g) in a glass ampoule for six hours at 65°. The excess of dibutylamine was removed under reduced pressure on a water bath at 50°. The solution was slightly acidified with hydrochloric acid, and the neutral products were extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding 11 g of unchanged methoxy ketones, b.p. 84-86° at 9 mm, n_D^{20} 1.4300. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-fractionated, yielding 2.5 g of the above-described amino ketone (XV), b.p. 107-109° at 7 mm; n_D^{20} 1.4620.

Preparation of the Amino Ketone (XVIII)

a) Dibutylamine (13 g) was added to 5-methyl-1,4-hexadien-3-one (XVI) (b.p. 70-73° at 70 mm; n_D^{20} 1.4740) (10 g) [5], and the temperature of the mixture rose to 70°. The mixture was then heated at 80° in a glass ampoule for 30 minutes. The excess of dibutylamine was removed under reduced pressure on a water bath at 50°. The reaction mixture was slightly acidified with hydrochloric acid and extracted with ether in order to remove neutral products, which, however, were almost absent (1 g). The organic base was salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding 12.5 g of 1-dibutylamino-5-methyl-4-hexen-3-one (XVIII), b.p. 123-125° at 4 mm; n_D^{20} 1.4600; d_4^{20} 0.8730; found MR 75.00; calculated MR 74.95.

Found %: N 6.01

$C_{15}H_{25}ON$. Calculated %: N 5.84

b) A mixture of 1-methoxy-5-methyl-4-hexen-3-one (b.p. 80-82° at 10 mm; n_D^{20} 1.4570) (15 g) [4], dibutylamine (11 g), and water (3 g) was heated in a glass ampoule for four hours at 80° and the reaction mixture was treated as in the previous experiment, yielding 2.1 g of the amino ketone (XVIII), b.p. 127-129° at 5 mm; n_D^{20} 1.4602.

Preparation of the Amino Ketone (XIX)

a) Freshly distilled amino ketone (XVIII) (4 g) was dissolved in alcohol (15 ml) and hydrogenated in presence of a platinum catalyst for eight hours. The volume of hydrogen absorbed was 430 ml, instead of the theoretically required 400 ml. The catalyst was filtered off, the alcohol was driven off, and vacuum fractionation of the residue yielded 1.9 g of 1-dibutylamino-5-methyl-3-hexanone (XIX), b.p. 102-103° at 2 mm; n_D^{20} 1.4500; d_4^{20} 0.8553; found MR 75.65; calculated MR 75.42.

Found %: N 5.32; 6.01

$C_{15}H_{31}ON$. Calculated %: N 5.80

b) Dibutylamine (7 g) and water (3 g) were added to 1-methoxy-5-methyl-3-hexanone (XX) (b.p. 64° at 11 mm; n_D^{20} 1.4190) (8 g) [8], and the mixture was heated in a glass ampoule at 80° for 2 hr 30 min. The excess of dibutylamine was removed under reduced pressure on a water bath at 50°. The solution was slightly acidified with hydrochloric acid, and the neutral products were extracted with ether. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled, yielding 3.7 g of the above-described amino ketone (XIX); b.p. 101-103° at 2 mm; n_D^{20} 1.4500.

SUMMARY

1. Under the influence of mercuric sulfate in methanol solution, tetrahydro 2-methyl-4-(vinylethynyl) pyran-4-ol (I) isomerizes into the divinyl ketone (II). The latter, under the conditions of the reaction writes

with methanol and gives the methoxy ketone (III), which, on hydrogenation, absorbs one molecule of hydrogen, yielding the saturated methoxy ketone (IV).

2. When methanol is caused to split from the unsaturated methoxy ketone (III), the divinyl ketone (II) is obtained in good yield.

3. By the action of aqueous solutions of dimethylamine and piperidine on the methoxy ketone (III), the amino ketones (V) and (VI) respectively are obtained.

4. By the action of diethylamine (or dibutylamine) on the ketone (VII) or the ketone (VIII), the amino ketone (IX) or (X) is formed.

5. By the action of diethylamine (or dibutylamine) on the ketones (XI), (XII), or (XIII), the diamino ketone (XIV) or (XV) is formed.

6. By the action of dibutylamine on the ketone (XVI) or the ketone (XVII), the amino ketone (XVIII) is obtained, and this, on being hydrogenated, absorbs one molecule of hydrogen and forms the saturated amino ketone (XIX), which is obtained also by the action of dibutylamine on the saturated methoxy ketone (XX).

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* See Consultants Bureau English translation, page 1833.

** See Consultants Bureau English translation, page 1643.

*** See Consultants Bureau English translation, page 413.

SYSTEMATICS OF MACROMOLECULAR COMPOUNDS

(NOMENCLATURE AND CLASSIFICATION OF MACROMOLECULAR COMPOUNDS)*

V. V. Korshak

Only in the last two decades has the chemistry of macromolecular compounds become a separate entity and taken shape as a section among other sections of organic chemistry. Being an independent branch of science, it is characterized, when compared with other sections of organic chemistry, by its much greater use of the methods of physics, and also of physical and colloid chemistry, for it constitutes in essence a synthesis of these sciences, among which the leading role is to be assigned to organic chemistry.

However, as the subject and field of the chemistry of macromolecular compounds are of such recent development, a number of fundamental questions determining its further progress have not yet been solved. Among such questions of a purely chemical character, the problem of the systematics of macromolecular compounds takes first place. The primary importance of dealing with problems of systematics results from the fact that work on the synthesis of new compounds can now no longer be based on those empirical principles that have hitherto prevailed. For further progress in this field it is essential to systematize and analyze the abundance of material that chemists have now accumulated. Only on this basis can further planned progress in the synthetic chemistry of high polymers be made. In this connection there is the question of the need for dealing with such preliminary problems as the nomenclature and classification of macromolecular compounds.

Nomenclature of Macromolecular Compounds

The names of macromolecular compounds have been formed hitherto in an unsystematic fashion. Natural compounds generally have their own names, which do not in any way reflect their structures. Examples are cellulose, starch, protein, inulin, lignin, etc.

Synthetic compounds are generally named after the starting substances from which they are obtained. Thus, all polymers are named after the starting substance, with the addition only of the prefix "poly", e.g. polyethylene, polystyrene, polyvinyl chloride, etc. In the case of polycondensation products, the word "resin" is added to the names of the starting substances, e.g. phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin, etc. As will be seen, in the majority of cases these names do not at all reflect the chemical structure of the macromolecular compound itself and therefore do not give any idea of the possible chemical reactions of the substance, and therefore of its properties.

Also, one and the same compound may have several names, corresponding to various starting substances from which it may be prepared. Thus, polyethylene oxide (the polymer of ethylene oxide) is called polyethylene glycol, if it is obtained from glycol. Polycaprolactam, obtained by the polymerization of caprolactam, may be obtained also by the polycondensation of aminocaproic acid, and should then be called polycaproadamide. The number of examples of this sort will, of course, grow ever greater as time goes on. This is a further proof of the

* Printed in accordance with the resolution of the Seventh All-Union Conference on Macromolecular Compounds, which took place in Moscow on June 12th, 1952. The basic principles of the proposed systematic scheme were reported at the Sixth All-Union Conference on Macromolecular Compounds, held June 21-25th, 1949 in Leningrad, and were published in a number of monographs [1,2,3] and articles [4,5].

The Seventh All-Union Conference on Macromolecular Compounds approved in principle the nomenclature and classification of macromolecular compounds published here, and the Conference resolved that it should be published in order that it might be discussed and that greater precision might be given to the basic ideas.

(NOTE: In view of the nature of this paper, the author's nomenclature is transcribed as closely as possible, i.e. is not adjusted to American practice, as in the remaining papers of this issue. — Publisher).

need for a nomenclature that is based in the first place on the structure of the macromolecular compound itself, and not on various preparative methods, the number of which may be fairly high.

The great need for a nomenclature based on chemical principles is generally recognized, a proof of which may be found in the appearance in 1952 of a new nomenclature, drawn up by a group of foreign chemists [6]. It must be pointed out, however, that, apart from their proposals relating to terms characterizing the physical properties of the polymers and their viscosity in solution, many of their proposed terms cannot be regarded as satisfactory, and this is particularly true of the chemical terminology of high polymers. Hence, the appearance of this nomenclature does not prompt us to withdraw the nomenclature for the naming of macromolecular compounds proposed by us considerably earlier (1949), which is expounded below.

The basis of our proposed rational nomenclature is the structure of the main chain of the macromolecule. The prefix "poly" will indicate that we have the name of a macromolecular compound. After the prefix will be placed a bracket, after which will be given the number and disposition of substituents; after each will be indicated the percent content, which is of importance in copolymers. In parentheses will be given the name of the fundamental repeating unit of the macromolecule chain.*

Examples of the names of a number of polymers are given below in Table 1.

TABLE 1

Examples of the Rational Names of Polymers

Formula	Name of polymer	
	Usual	Rational
$\dots -CH_2-\dots$	Polyethylene	Poly(methylene)
$\dots -CH-CH_2-\dots$ C_6H_5	Polystyrene	Poly[phenyl(ethylene)]
$\dots -CH-CH_2-\dots$ Cl	Polyvinyl chloride	Poly[chloro(ethylene)]
$\dots -C-CH_2-\dots$ Cl Cl	Polyvinylidene chloride	Poly[1,1-dichloro(ethylene)]
$\dots -CH_2-C=CH-CH_2-\dots$ CH ₃	Rubber	Poly[2-methyl(buten-2-ylene-1,4)]
$\dots -NH(CH_2)_5CO-\dots$	Polycaprolactam	Poly[amino-1-caproylene-1,7]
$\dots -O(CH_2)_2-\dots$	Polyethylene oxide	Poly(hydroxyethylene)

We shall confine ourselves to these examples, which illustrate sufficiently clearly the principles of this nomenclature. The names of a large number of polymers will be given later in Tables 2-6, when describing the classification of macromolecular compounds.

It must be made clear, however, that the use of rational names in no way excludes the use of the common names of polymers that are already a part of chemical language. Trivial names often have the advantage of greater brevity, particularly in the case of natural compounds for the naming of compounds such as cellulose, protein, lignin, inulin, etc., and this alone justifies their further use. There are names in use, however, which are contrary to all principles of chemical nomenclature and should no longer be used, being completely incorrect. Examples of such names are "polychlorovinyl", "polychlorovinylidene", "perchlorovinyl", etc. These names must be replaced, respectively, by polyvinyl chloride, polyvinylidene chloride, chlorinated polyvinyl chloride, etc., or by the corresponding rational names: poly[chloro(ethylene)], poly[1,1-dichloro(ethylene)], etc.

In our examination of classification, we shall use these rational names in addition to generally accepted names.

Classification of Macromolecular Compounds

Questions relating to the classification of macromolecular compounds have been considered by many chemists.

* There is as yet no consistent nomenclature for bivalent radicals. By analogy with ethylene we form their names by addition of the ending "ylene".

Thus, Carothers [7] divided them into two classes:

1. Polymers of the additive type, or A-polymers. This class comprises substances for which the formula of the monomer is identical with the formula of the structural unit of the polymer. In this class he placed: polyolefins, polyoxymethylenes, polystyrenes, rubber, etc.

2. Polymers of the condensation type, or C-polymers. In this class the composition of the monomer is not identical with that of the structural unit of the polymer. This class includes esters of polyhydric alcohols with polybasic acids, phenol-aldehyde resins, urea-aldehyde resins, etc.

Kienle [8] took the behavior of synthetic resins when heated or treated with reagents as the basis of his classification; he distinguished three groups:

1. Thermoreactive resins. These are resins that are converted by heat into an infusible condition; they include resins based on glycerol and polybasic acids, acetylene derivatives, polyolefin resins, pheno'- and urea-aldehyde resins, etc.

2. Thermoplastic resins. These are resins that do not change on being heated and do not lose their plastic properties; they include polystyrene, polyvinyl acetate, polyethylene, condensation products formed by glycols with dicarboxylic acids, etc.

3. Element-reactive resins. These are resins that go into an infusible condition under the action of elements such as oxygen or sulfur. This group includes resins prepared from glycerol and polybasic acids together with drying oils, sulfur-olefin resins, etc.

Morgan, Megson, and Holmes [9] divide these compounds into two groups:

1. Condensation resins, which solidify, being converted into infusible, insoluble products.

2. Polymerization resins, the polymerization products from unsaturated compounds; they are not able to go into an infusible condition.

Petrov, Rutovsky, and Losev [10] take the chemical reactions used in the preparation of synthetic resins as their basis and divide them into the following groups:

1. Plastics based on condensation products (phenol- and urea-aldehyde, polyamide resins).

2. Plastics based on polymerization products (polystyrene, polyethylene, etc.).

3. Plastics based on esters and ethers of cellulose.

4. Plastics based on proteins.

5. Plastics based on natural and artificial bitumens.

6. Plastics based on the oxidation products of the glycerides of unsaturated fatty acids.

Fischer [11] divides all synthetic polymers into two groups: elastomers and plastomers. Elastomers are subdivided into:

1. Elastoprenes (polybutadiene, polyisoprene, etc.).

2. Elastolenes (polyisobutene).

3. Elastothiomers (thiokols).

4. Elastoplastics (polyacrylates, polyvinyl acetate, etc.).

Plastomers are subdivided into:

1. True thermoplastics (shellac, polystyrene, celluloid, etc.).

2. Plastics that solidify when heated (phenol-formaldehyde resins, glyptals, etc.).

Meyer [12] divides all macromolecular compounds into the following seven groups:

1. Inorganic high polymers (sulfur, selenium, graphite, diamond, silicon, boron, silica, polyphosphonitrile chloride, glass, etc.).

2. Macromolecular hydrocarbons (polyvinyl esters, alcohols, acids, polystyrene, rubber, chloroprene, etc.).

3. Polymeric ethers, sulfides, etc. (polyoxymethylenes, polyethylene oxide, glyptals, polysulfides, polyamides, phenol-formaldehyde, urea-formaldehyde, and aldehyde resins, etc.).

4. Cellulose and its derivatives.

5. Substances associated with cellulose (lignin, gums, etc.).

6. Starch.

7. Proteins.

Staudinger [13] classified organic compounds according to molecular weight and number of carbon atoms in the molecule into a number of groups, which are given in Table 2.

TABLE 2

Staudinger's Classification of Organic Compounds

Substances	Molecular weight	No. of carbon atoms in molecule
A. Low-molecular-weight organic compounds; completely homogeneous substances	16-5000	1-500
B. "The world of every-day molecules"; polymeric and constitutionally homologous substances:		
1. Semicolloids	1000-10000	100-1000
2. Eucolloids	10^4-10^6	10^3-10^5
3. Macromolecular insoluble substances	10^4-10^x	10^3-10^{x-1}
4. Diamond (1 g)	$6.06 \cdot 10^{23}$	$5 \cdot 10^{22}$

In this way he divided all organic compounds into two groups (low- and high-molecular-weight compounds). The first group contains those which can be obtained in a pure, homogeneous state, and the second group contains those which are built up of macromolecules and can be obtained only in polymerically homogeneous state, i.e. as a mixture of polymer-homologs. The macromolecular substances are divided in their turn into four groups: semicolloids, eucolloids, insoluble substances, and three-dimensional substances. At the basis of this subdivision lies the solubility of the substance and the properties of its solution: Semicolloids are readily powdered substances that dissolve without swelling; their dilute solutions are of low viscosity and obey the Hagen-Poiseuille law.

Eucolloids are solid substances that swell before dissolving; their solutions are very viscous and behave abnormally during efflux. The molecules of eucolloids have chain lengths of greater than 3000 A. Insoluble macromolecular substances have longer chains (1,000,000 A and greater) and are therefore unable to go into solution. Three-dimensional macromolecular substances, the most typical example of which is diamond, are also insoluble, but from another cause: their crystal lattices extend in space owing to the fact that individual chains are firmly attached to one another by a large number of cross links and cannot be separated without rupture of these links.

Staudinger made a further subdivision of the group of soluble macromolecular substances into three groups: homopolar, heteropolar, and coordination compounds. The first contains rubber, polystyrene, cellulose acetate, and similar neutral substances. The second contains the phosphonium salts of rubber, which contain a macromolecular cation, and also sodium polyacrylate and complex compounds formed by cellulose with the cuprammonium salt in Schweizer's solution, which contain macromolecular anions. To this group also belong the proteins, which are amphoteric macromolecular compounds. To the coordination group he assigns polyvinyl alcohol, polyacrylic acid, cellulose, starch, lichenin, and other similar compounds.

Apart from these, many more classifications have been proposed based on a great variety of criteria [14].

This short survey shows that the abundance of proposed variants, while undoubtedly indicating that the need for correct classification is widely felt, is at the same time an indication that the proposed methods are not regarded as wholly satisfactory.

It is, in fact, true that, at the present time, a large number of investigations, aimed at the discovery of

new macromolecular substances, the elucidation of their structures, and the study of their properties, are providing an enormous amount of material that has not yet been systematized within any definite plan. The literature on macromolecular compounds regards and classifies these compounds, as we have seen, on the basis of casual and mainly arbitrary criteria, such as their origin, the starting substances, their physical properties, etc.

The attempts at generalization that have taken place up to the present time have generally related to particular narrow classes, such as vinyl compounds, cellulose, rubber, etc., and have thus not brought any order into the whole enormous field of macromolecular compounds, which comprises a great accumulation of experimental material, which is linked together only in a casual way.

It is quite clear that for a classification of macromolecular compounds to be fruitful and useful, its basis must rest on an invariable criterion, such as the structure of the macromolecular compound itself. Only then can a system be created that will correctly portray the interrelations of already known macromolecular substances, make it possible to predict new compounds, and so act as a leading thread in scientific investigations. All other methods of coordinating macromolecular substances, based on classification by starting substances, by methods of preparation, etc., can have only subsidiary significance. Directed by these considerations, we made an attempt to make a system of classification of macromolecular compounds having as its basis the structure of the actual chain, which in the case of high polymers may be equivalent to the structure of the essential repeating units of which the chain of the macromolecule is built up.

Principles of the Chemical Classification of Macromolecular Compounds

At the basis of the classification of macromolecular compounds we place the structure of the main chain, and also the presence of substituents, their number, nature, and disposition. All macromolecular compounds can then be grouped into two large classes:

1. Substances having chains that are built up from the atoms of one element only (homochain compounds). When the element is carbon, they will be carbochain compounds; when it is sulfur, they will be sulfidochain compounds, when it is arsenic they will be arsenochain compounds, and so on. Examples of carbochain compounds are polymerization products from unsaturated compounds, such as rubber, polyvinyl chloride, polyethylene, etc.
2. Substances having chains that include atoms of carbon, oxygen, nitrogen, sulfur, silicon, and other elements. This class we shall call heterochain compounds. Examples of compounds of this class are thiokol, cellulose, proteins, organosilicon polymers, etc.

The distinction between these classes appears most clearly in their chemical properties, particularly in the resistance of compounds of the first class to hydrolysis and the tendency of substances of the second class to be destroyed by hydrolyzing agents. Each of these main classes can be subdivided into groups according to the structure of the chain, the presence of double bonds in the chain, and, in the case of the second class, on the number and nature of the hetero atoms. Thus, in the first class, carbochain compounds, we shall have the following groups:

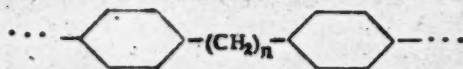
1. Polymethylene group



2. Unsaturated chain group

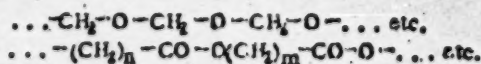


3. Cyclochain group

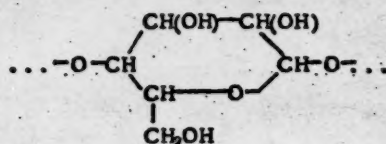


In the second class we shall have the following groups:

1. Oxygen-containing chains (polyethers)

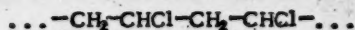


2. Nitrogen-containing chains (structure analogous to preceding).
3. Sulfur-containing chains (structure analogous to first group).
4. Ring- and oxygen-containing chains (cellulose, starch, etc.).

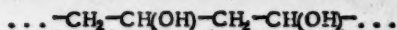


Each of these groups is divided in its turn into subgroups according to what side groups are present, their nature, number, disposition, etc.; for example, the first group of the carbochain class will contain the following subgroups:

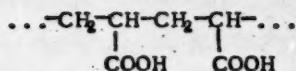
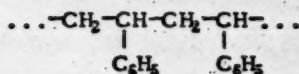
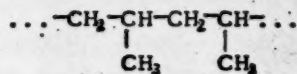
a) halogen compounds



b) hydroxy compounds



c) compounds having side chains of various structures



These examples give a sufficiently clear illustration of the basic elements of the proposed system for the classification of macromolecular compounds.

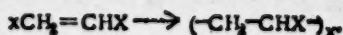
An essential element that must appear in the system is the quantitative characterization: the "degree of substitution", which indicates the number of substituents in the chain calculated for a definite number of carbon atoms (for example, 100); we shall represent it by the index "d_s". This index may change within wide limits: from 0 for polyethylene to 100 for polytetrafluoroethylene. This index can be applied usefully also to the case of copolymers. For heterochain compounds it is expedient to introduce the concept of "heterochain characteristic", which will be denoted by the index "h_c" and which indicates the number of hetero atoms per 100 atoms in the chain. This index is 100 for thiokol, 50 for formaldehyde polymers, 33 for the polymer of ethylene oxide, and so on.

Below we give the basis of the scheme for the chemical classification of macromolecular compounds.

A. Carbochain Compounds

We shall give the name of carbochain compounds to all macromolecular compounds in which the macromolecule chain is composed only of carbon atoms, and so distinguish them from heterochain compounds, in which the chain contains also hetero atoms (oxygen, nitrogen, sulfur, etc.). Carbochain compounds constitute a large class of macromolecular compounds, the numerous members of which contain a great variety of substituents. In this class are found compounds, such as natural and various forms of synthetic rubber, polystyrene, polyvinyl chloride, and many others, which are widely applied in various branches of industry.

The principal method for the preparation of carbochain compounds consists in the polymerization of unsaturated hydrocarbons or their derivatives occurring by way of the opening of double bonds and formation of the straight chain of the macromolecule:



Certain carbochain compounds may be obtained also by a polycondensation reaction from dihalo derivatives by the action of alkali metals:



TABLE 3

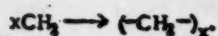
Saturated Carbochain Macromolecular Compounds

Group	Subgroup	Example		Formula
		Name		
		rational	usual	
1	2	3	4	5
Hydrocarbons	No substituent	Poly(methylene)	Polyethylene	$\dots -CH_2-CH_2-\dots$
"	Monoalkyl-substd.	Poly[1-methyl(ethylene)]	Polypropylene	$\dots \begin{array}{c} CH-CH_2- \\ \\ CH_3 \end{array} \dots$
"	Monoaryl-substd.	Poly[1-phenyl(ethylene)]	Polystyrene	$\dots \begin{array}{c} CH-CH_2- \\ \\ C_6H_5 \end{array} \dots$
"	"	Poly[naphthylene-(ethylene)]	Polyacenaphthene	$\dots \begin{array}{c} CH-CH- \\ \quad \\ \text{Naphthalene ring} \end{array} \dots$
"	"	Poly[phenyleneoxy-(ethylene)]	Polycoumarone	$\dots \begin{array}{c} CH-CH- \\ \quad \\ \text{Coumarone ring} \end{array} \dots$
"	"	Poly[benzylene(ethylene)]	Polyindene	$\dots \begin{array}{c} CH-CH- \\ \quad \\ \text{Indene ring} \end{array} \dots$
"	Dialkylsubstd.	Poly[1,1-dimethyl-(ethylene)]	Polyisobutylene	$\dots \begin{array}{c} CH_3 \\ \\ -C-CH_2- \\ \\ CH_3 \end{array} \dots$
Halosubstd.	Monohalo-substd.	Poly[chloro(ethylene)]	Polyvinyl chloride	$\dots \begin{array}{c} CH-CH_2- \\ \\ Cl \end{array} \dots$
"	"	Poly[bromo(ethylene)]	Polyvinyl bromide	$\dots \begin{array}{c} CH-CH_2- \\ \\ Br \end{array} \dots$
"	"	Poly[iodo(ethylene)]	Polyvinyl iodide	$\dots \begin{array}{c} CH-CH_2- \\ \\ I \end{array} \dots$
"	"	Poly[fluoro(ethylene)]	Polyvinyl fluoride	$\dots \begin{array}{c} CH-CH_2- \\ \\ F \end{array} \dots$
"	Dihalosubstd.	Poly[1,1-dichloro-(ethylene)]	Polyvinylidene chloride	$\dots \begin{array}{c} Cl \\ \\ -C-CH_2- \\ \\ Cl \end{array} \dots$
"	"	Poly[1,1-dibromo-(ethylene)]	Polyvinylidene bromide	$\dots \begin{array}{c} Br \\ \\ -C-CH_2- \\ \\ Br \end{array} \dots$

TABLE 3 -- (Continued)

Group	Subgroup	Example		Formula
		Name		
		rational	usual	
Halosubstd.	Tetrahalo-substd.	Poly[tetrafluoro-(ethylene)]	Teflon	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \cdots - \text{C} - \text{C} - \cdots \\ \quad \\ \text{F} \quad \text{F} \end{array}$
	"	Poly[trifluorochloro-(ethylene)]	Polytrifluorochloroethylene	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \cdots - \text{C} - \text{C} - \cdots \\ \quad \\ \text{Cl} \quad \text{F} \end{array}$
Alcohols	Monohydric alcohols	Poly[hydroxy(ethylene)]	Polyvinyl alcohol	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{OH} \end{array}$
Ethers	Monoalkyl ethers	Poly[alkoxy(ethylene)]	Polyvinyl alkyl ether	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{OR} \end{array}$
Esters	Monocarboxylic esters	Poly[acetoxymethyl(ethylene)]	Polyvinyl acetate	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{OCOCH}_3 \end{array}$
Amines	Monoamines	Poly[amino(ethylene)]	Polyvinylamine	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{NH}_2 \end{array}$
	"	Poly[carbazolyl(ethylene)]	Polyvinylcarbazole	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{N} \\ \text{C}_6\text{H}_4 \end{array}$
Nitro Compound	Mononitro Compounds	Poly[nitro(ethylene)]	Polynitroethylene	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{NO}_2 \end{array}$
Carboxylic acids	Monocarboxylic acids	Poly[carboxy(ethylene)]	Polyacrylic acid	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{COOH} \end{array}$
	"	Poly[1-methyl-1-carboxy-(ethylene)]	Polymethacrylic acid	$\begin{array}{c} \text{CH}_3 \\ \\ \cdots - \text{C} - \text{CH}_2 - \cdots \\ \\ \text{COOH} \end{array}$
Carboxylic esters	Monocarboxylic esters	Poly[carboxymethyl-(ethylene)]	Polymethyl acrylate	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{COOCH}_3 \end{array}$
	"	Poly[1-methyl-1-carboxymethyl(ethylene)]	Polymethyl methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \cdots - \text{C} - \text{CH}_2 - \cdots \\ \\ \text{COOCH}_3 \end{array}$
Nitriles	Mononitriles	Poly[cyano(ethylene)]	Polyacrylonitrile	$\begin{array}{c} \cdots - \text{CH} - \text{CH}_2 - \cdots \\ \\ \text{CN} \end{array}$

A third method for the preparation of carbochain compounds consists in the polymerization of bivalent free radicals. This method is still quite new and has been developed only in its application to the case of the preparation of polymethylene by the polymerization of methylene radicals:



In this case the methylene radicals are obtained by the decomposition of diazomethane or by the reduction of carbon monoxide.

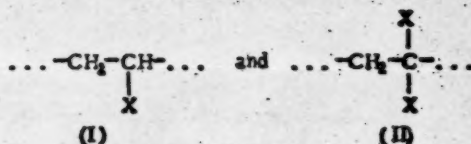
In the future, no doubt, when methods for the preparation of the necessary free radicals have become more perfect, this method will receive wide development.

According to the structure of the carbon chain, carbochain compounds may be divided into three groups:

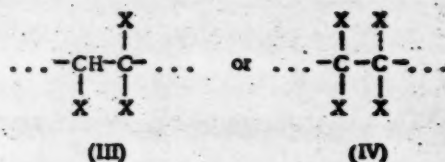
- A. compounds having a saturated chain;
- B. compounds having an unsaturated chain; and
- C. compounds having nuclei in the chain.

Further subdivision is done in accordance with the number and nature of substituents in the macromolecule: hydrocarbons containing alkyl and aryl groups, halogen derivatives, alcohols, amines, acids, etc.

It should be noted that the number of possible compounds of these types is considerably greater than the number already known. This is to be explained on the one hand by the fact that this class of substances became an object for systematic study only comparatively recently, and on the other hand by the fact that the methods known at present for the preparation of carbochain compounds are not suitable for the synthesis of certain groupings. Thus, the polymerization method will yield fairly readily numerous compounds having one and sometimes two substituents of the types:



whereas this method, owing to steric hindrance, is in most cases unsuitable for the preparation of compounds containing three or four substituents in the unit [15], i.e. of the types:



For this reason, the compounds at present known are mainly of Type (I) and, to a less extent, of Type (II); there are very few compounds of Types (III) and (IV).

For the purpose of illustration, the representatives of the group of saturated carbochain compounds known at the present time are given in Table 3.

The second group of carbochain compounds, the unsaturated compounds, are generally prepared by the polymerization of diolefins having conjugated double bonds. The main representatives of the group of unsaturated carbochain compounds are given in Table 4.

The third group of carbochain compounds are compounds having, as components of their chains, cyclic residues, such as phenyl or cyclohexyl groups having various substituents. These compounds are prepared by the polycondensation of dihalo-substituted hydrocarbons or aldehydes with benzene, its homologs, and its derivatives. The main representatives of this group of compounds are given in Table 5.

B. Heterochain Compounds

We shall give the name of heterochain compounds to all macromolecular compounds that have macromolecular chains consisting not only of carbon atoms or of the atoms of any other single element, but also of atoms of various other elements (oxygen, nitrogen, sulfur, silicon, etc.).

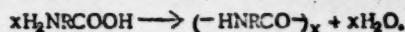
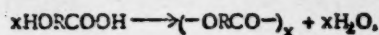
TABLE 4

Unsaturated Carbochain Macromolecular Compounds

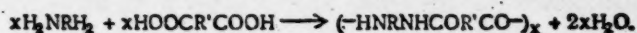
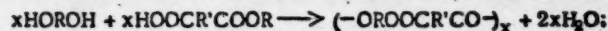
Group	Subgroup	Example		
		Name		Formula
		rational	usual	
Unsatd. carbo-chain hydrocarbons	No substituent	Poly[buten-2-ylene-1,4]	Polybutadiene	$\dots -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\dots$
"	Monoalkyl-substd.	Poly[2-methyl(buten-2-ylene-1,4)]	Rubber	$\dots -\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2-\dots$
"	Dialkylsubstd.	Poly[2,3-dimethyl(buten-2-ylene-1,4)]	Polydimethylbutadiene	$\dots -\text{CH}_2-\underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}=\text{C}-\text{CH}_2-\dots$
Halosubstd.	Monohalo-substd.	Poly[2-chloro(buten-2-ylene-1,4)]	Polychloroprene	$\dots -\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2-\dots$

The heterochain compounds comprise a large class of macromolecular compounds, the numerous members of which contain not only various atoms of other elements (hetero atoms) in various combinations with a variable number of carbon atoms, but also a variety of substituents.

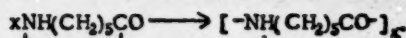
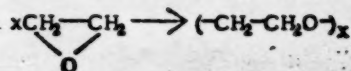
This class contains natural substances such as cellulose, proteins, and inulin, and also various synthetic products, such as polyesters, polyamides, polyanhydrides; there are many others, playing a great part in the life of animals and plants and having application on a very large scale in various branches of industry. The principal method of preparing heterochain compounds is by the polycondensation of various bifunctional compounds containing two different groups in their molecules, for example, hydroxy acids, amino acids, etc.



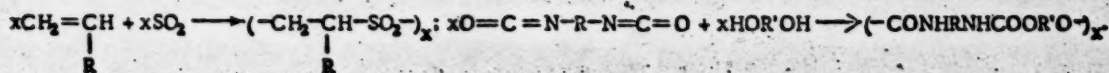
or by the polycondensation of various bifunctional compounds with other bifunctional compounds, for example, dicarboxylic acids with glycols, diamines, etc.



Heterochain macromolecular compounds may be obtained also by the polymerization of heterocyclic compounds such as ethylene oxide, ethyleneimine, caprolactam, caprolactone, etc.



A third method of preparation is the reaction of copolymerization of compounds such as sulfur dioxide with olefins, diazocyanates with glycols or diamines, etc.



Heterochain macromolecular compounds may be divided, in accordance with the structure of the carbon chain, into the following groups:

- A. compounds having a saturated straight chain;
- B. compounds having an unsaturated straight chain; and
- C. compounds having rings in the chain.

Further subdivision into subgroups is in accordance with the number and nature of the substituents entering into the composition of the chain: compounds having oxygen atoms in the chain, those having nitrogen atoms, sulfur atoms, etc.

Group	Subgroup	Example		Formula
		Name		
		rational	usual	
Hydrocarbons having hydroaromatic nuclei	Without methylene groups	Poly(cyclohexamethylene)	—	
	With one methylene group	Poly(cyclohexamethylenemethyl)	—	
	With two methylene groups	Poly(cyclohexamethyleneethyl)	—	
Hydrocarbons having aromatic nuclei	Without methylene groups	Poly[phenylene-1,4]	—	
	With one methylene group	Poly[phenylene-1,4-methyl]	—	
	With two methylene groups	Poly[phenylene-1,4-ethyl]	—	
	With three methylene groups	Poly[phenylene-1,4-propyl]	—	
Phenols	With one methylene group	Poly[2-hydroxy(phenylene-1,3-methyl)]	Phenol-formaldehyde resin	
	With one methylene group, monoalkylsubstit.	Poly[2-hydroxy-1'-methyl(phenylene-1,3-methyl)]	Phenol-acetaldehyde resin	

The heterochain compounds constitute a class of substances that is very varied with respect to structure and very large with respect to the number of known representatives. Apart from the large number of natural compounds of this type, a very great number of synthetic heterochain compounds are known at the present time which are distinguished by a number of interesting properties and have found practical application. Although synthetic methods for the preparation of compounds of this class are only in the early stages of development, it is already possible to foresee far-reaching developments in the synthesis of various heterochain compounds in the near future. In order fully to characterize the significance of heterochain compounds, it is necessary to consider the exceptional part that they play in the life of the living cell, where it may be the skeletal material (cellulose), the reverse of nutritive material (starch, inulin), or the basic material substrate of the living cell (protein).

Individual groups of linear heterochain compounds are given in Table 6.

As we have given an exposition only of the principles of chemical classification, we have not touched on such questions as two- and three-dimensional structures of various types, branched chains, etc. There is no doubt, however, that it is possible to include them in this system. It must be added that, since all properties of macromolecular compounds are determined by the structure of the main chain of the macromolecule, the whole complex

TABLE 6

Heterochain Macromolecular Compounds

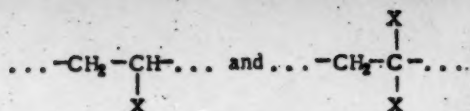
Group	Subgroup	Example		
		Name		Formula
		rational	usual	
Oxygen-containing compounds	Ethers	Poly(hydroxymethylene)	Paraform	$\dots -OCH_2-\dots$
	"	Poly(hydroxyethylene)	Polyethylene oxide, polyethylene glycol	$\dots -OCH_2CH_2-\dots$
	Esters	Poly(hydroxycaproylene)	Polycaprolactone	$\dots -O(CH_2)_5CO-\dots$
	"	Poly(ethyleneadipate)	Polyethylene adipate	$\dots -O(CH_2)_2OCO(CH_2)_4CO-\dots$
Nitrogen-containing compounds	Polyamines	Poly(aminoethylene)	Polyethylenimine	$\dots -NHCH_2CH_2-\dots$
	Polyamides	Poly(amino-caproylene)	Polycaprolactam	$\dots -HN(CH_2)_5CO-\dots$
	"	Poly(hexamethyleneadipamide)	Polyhexamethyleneadipamide	$\dots -NH(CH_2)_6NHCO(CH_2)_4CO-\dots$
	Polyhydrazones	Poly(diphenylenediacyl-dihydrazone)	Polyhydrazone	$\dots =NNH \text{ (cyclohexane ring) } NHN=C-C=\dots$ <div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;">CH_3</div> <div style="margin-right: 10px;">CH_3</div> </div>
Sulfur-containing compounds	Polysulfides	Poly(tetra-thioethylene)	Thiokol	$\dots -S_4CH_2CH_2-\dots$

of physical and chemical properties peculiar to a given compound may be expressed as a function of the structure. Chemical properties, in fact, depend on the nature and number of substituents (chlorine, hydroxyl, alkoxy, carboxyl, carbalkoxyl, alkyl, aryl, etc.) and on the structure of the macromolecular chain itself (presence in the chain of atoms of oxygen, sulfur, nitrogen, etc., and also of various groupings, $C=C$, rings, etc.). All these atoms and groupings constitute the weak places in the molecule that are most inclined to enter into chemical reactions, and it is these that condition those properties of the substance that are functions of the reactions that occur (stability to acids, alkalis, oxidizing agents, heat, etc.).

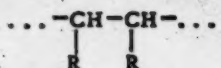
These same atoms and groupings, together with the general length and structure of the macromolecule, determine also the whole of that complex of properties that are generally called physical (solubility, stability to frost, thermal stability, plasticity, elasticity, hardness, etc.). They are the source also of forces of interaction between separate chains, i.e. of the magnitude of that effect that used to be called Van der Waals forces, but which is now frequently associated with peculiarities of structure and is explained by the presence of various groups that participate in the formation of various specific chemical bonds.

The further, more detailed development of questions in systematics will doubtless be a matter for the future. But even now, it may be remarked that the proposed systematic scheme enables us to form a picture of the whole immense variety of macromolecular compounds, the possibility of whose existence follows from the structural teaching of Butlerov, and to compare them with the few substances that are at present known to us.

It is quite clear that one of the reasons for this is the paucity of methods used at present for the preparation of macromolecular compounds. Thus, polymerization permits us to prepare only those polymers that have one or, occasionally, two substituents in each ethylene residue [16], i.e. of the type:



Only rarely does this method permit the preparation of polymers having a substituent on each carbon atom, i.e. of the type:



And it is almost impossible to prepare, by this method, polymers having three or four substituents in the ethylene residue (only two such cases are known, the polymers of trifluorochloro- and tetrafluoroethylene), owing to steric hindrance [16].

Polycondensation appears to be the more universal method, but here also various limitations are encountered: thus in the case of five- and six-membered units, cyclic low-molecular-weight substances are formed more readily than polymers. The equilibrium nature of the process and reactions such as these make it difficult to obtain products of high molecular weight.

These difficulties can evidently be overcome by developing polymerization and polycondensation methods and also by seeking methods for the preparation of macromolecular compounds that are new in principle and are free from the limitations from which the present methods suffer.

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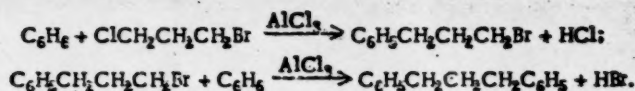
* This reference evidently contains a typographical error. No paper by Korshak appears in the indicated issue. -Pub.

MACROMOLECULAR COMPOUNDS [1]

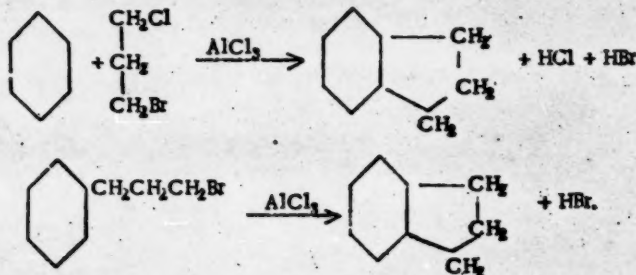
COMMUNICATION 53. POLYCONDENSATION OF 1-BROMO-3-CHLOROPROPANE WITH BENZENE

G. S. Kolesnikov and V. V. Korshak

We have previously [2] studied the polycondensation reaction of 1,2-dichloroethane with benzene in presence of aluminum chloride, and have established the main features of this reaction. However, the condensation with benzene of aliphatic halogen compounds having more than two methylene groups between the halogen atoms has received very little study. Thus, the condensation of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride has been described by Tsukervanik and Yatsimirsky [3], who studied the effect of temperature on the rate of formation of 1,3-diphenylpropane and the possibility of obtaining an alkylhalobenzene. On the basis of their results they concluded that the reaction of 1-bromo-3-chloropropane goes in two stages. First of all, (3-bromopropyl)benzene is formed, and this then reacts with a second molecule of benzene, yielding 1,3-diphenylpropane:

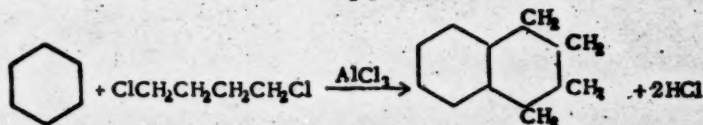


It was shown that at 6-12° the first reaction predominates, and (3-bromopropyl)benzene was isolated from the reaction products, but at higher temperatures (80-85°) the rate of the second reaction increases to such an extent that it is not possible to isolate (3-bromopropyl)benzene, and 1,3-diphenylpropane is the main reaction product. The authors pointed out the possibility of the formation of indan by the reaction of 1-bromo-3-chloropropane with benzene in accordance with the following schemes:



but Tsukervanik and Yatsimirsky did not isolate indan: they noted the formation of a resin, which was not investigated further.

The condensation of 1,4-dichlorobutane with benzene in presence of aluminum chloride yields 1,2,3,4-tetrahydronaphthalene as principal reaction product [4]:



We have undertaken a study of the polycondensation of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride. Two series of experiments have been carried out. In the first series, which had the object of determining the optimum amount of catalyst, the ratio of benzene to 1-bromo-3-chloropropane was maintained constant, and the amount of aluminum chloride was varied. The duration of the experiment and the temperature were the same in all cases. The molecular weights of the macromolecular reaction products were determined viscosimetrically. The results obtained are given in Table 1.

TABLE 1

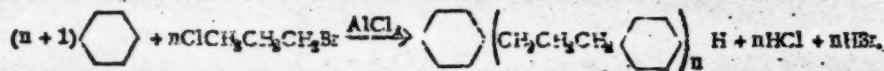
Effect of Catalyst Concentration on Yield and Molecular Weight of Polycondensation Product (benzene: 1-bromo-3-chloropropane = 1.3)

Concen. of aluminum chloride (mole-% with respect to benzene)	Macromolecular condensation product	
	Yield (% of 1-bromo-3-chloropropane)	Mol. weight
3	10.2	1980
12	18.5	3090
24	32.0	3070
30	50.5	3910
36	55.7	3810

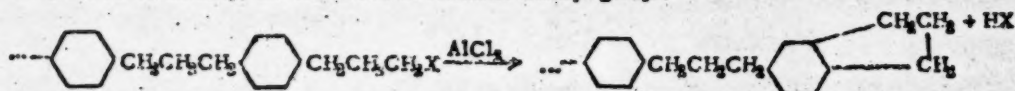
yield and molecular weight of the polycondensation products, the concentration of catalyst was maintained constant at 36 mole-% with respect to benzene. The amount of benzene, the temperature, and the duration of the reaction were maintained constant, and the amount of 1-bromo-3-chloropropane was varied. The polycondensation was carried out both in presence of excess of benzene and also in presence of excess of 1-bromo-3-chloropropane. The results obtained are given in Table 2.

It will be seen from Table 2 that with decrease in the excess of benzene the molecular weight of the polycondensation products rises at first, but then falls, products of maximum molecular weight being obtained with an excess of benzene in the region of 30-50 mole-%. On the basis of the theory of linear polycondensation that one of us has developed [5] it would be expected that products of maximum molecular weight would be formed when the reacting substances are present in equimolecular proportions but this is not so in the present case. This discrepancy may be explained as follows.

When there is a large excess of benzene, the main reaction is the formation of a linear polycondensation product:

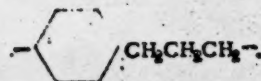


As the excess of benzene is reduced, an ever-increasing effect is shown by a side reaction, proceeding simultaneously with the main reaction, namely, the formation of terminal indanyl groups:



The probability of the formation of such indanyl groups naturally increases as the concentration of 1-bromo-3-chloropropane in the reaction mixture rises. The terminal indanyl groups so formed react with difficulty, or not at all, with 1-bromo-3-chloropropane, for the benzene ring of the indan is already substituted in three positions. As soon as the rate of formation of indanyl terminal groups becomes greater than the rate of formation of linear polycondensation products, the molecular weight of these products will decrease, and this decrease in molecular weight will be the greater, the greater the concentration of 1-bromo-3-chloropropane. When the linear condensation product

The yield was calculated on 1-bromo-3-chloropropane, it being assumed that one molecule of 1-bromo-3-chloropropane can give one phenylenepropyl residue:



It will be seen from Table 1 that at 30-36 mole-% of aluminum chloride the yield and the molecular weight of the polycondensation products become practically constant. Hence, in the second series of experiments, which had the object of determining the effect of the relative amounts of reacting substances on the

TABLE 2

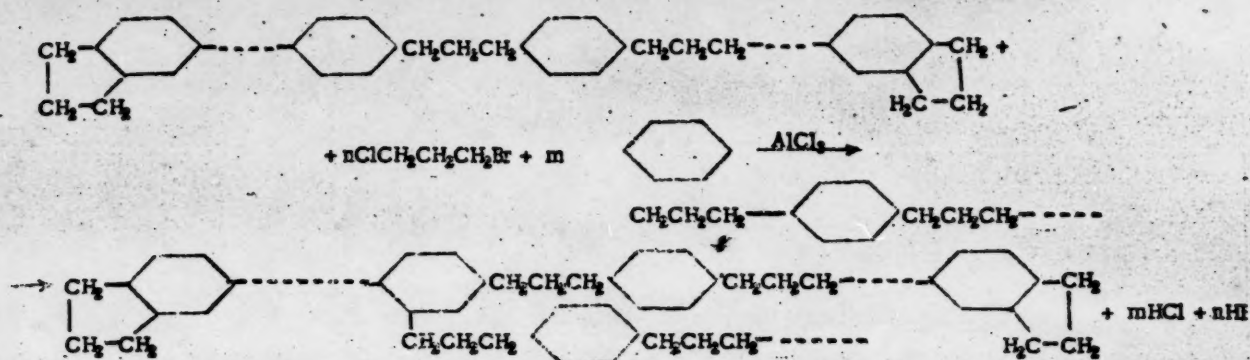
Polycondensation of 1-Bromo-3-chloropropane with Benzene (aluminum chloride concn.: 36 mole-% with respect to benzene)

Excess of benzene (mole-%)	Excess of 1-bromo-3-chloropropane (mole-%)	Macromolecular condensation product	
		Yield (%)	Mol. wt.
100	—	39.0*	2800
70	—	39.0*	2460
50	—	47.2*	3940
30	—	55.7*	3810
10	—	45.9*	2650
—	—	56.1*	2070
—	22	66.8**	2310
—	42	61.2**	2080
—	100	84.8**	1950

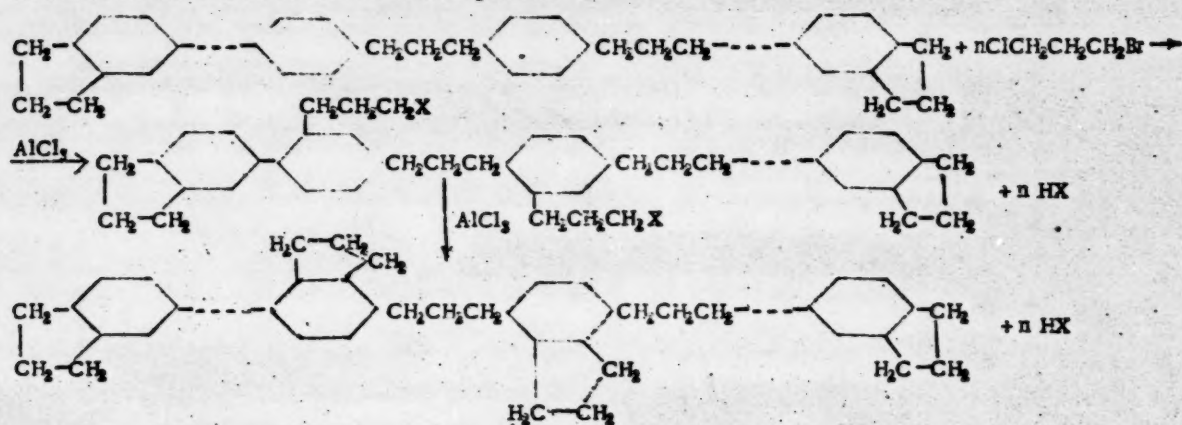
* With respect to 1-bromo-3-chloropropane

** With respect to benzene

has an indanyl group at each end (which occurs when there is an excess of 1-bromo-3-chloropropane), it will react with 1-bromo-3-chloropropane and benzene with formation of side chains:



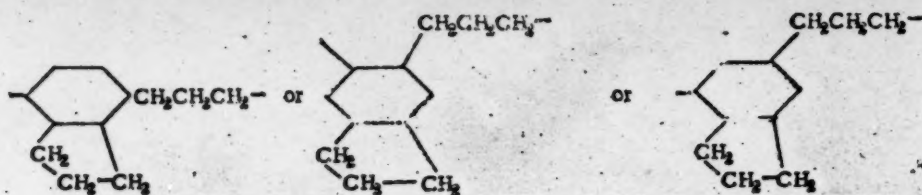
The side chains also may terminate with indanyl groups. The increase in molecular weight due to side-chain formation is not reflected in the molecular weight, as found by the viscosimetric method, which gives an estimate of the maximum size of the molecule. When there is a large excess of 1-bromo-3-chloropropane, indan residues may be formed in the chain of the linear condensation product:



Hence, arresting of chain growth in the polycondensation of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride is evidently due to the formation of terminal indanyl groups; the low molecular weight of the polycondensation products arises from this cause.

In order to determine the structure of the polycondensation product, we subjected it to destructive oxidation, as we did in the case of polyphenyleneethyl [6]. However, when oxidation was effected by means of chromic acid or by means of acid or alkaline potassium permanganate, it was not found possible to isolate oxidation products in amounts sufficient for the simplest estimations. Only by oxidation with nitric acid (sp. gr. 1.1, warm), and then further oxidation with potassium permanganate in alkaline medium, was it possible to isolate, as principal oxidation product, terephthalic acid, which was identified by its sublimation temperature, its equivalent weight as an acid, and the melting point of its dimethyl ester. In addition to terephthalic acid, an acid was obtained in insignificant amount for which the melting point and equivalent weight were determined; it was not investigated further. On the basis of these determinations this acid is probably *p*-benzenediacetic acid.

The obtaining of terephthalic and *p*-benzenediacetic acids as destructive-oxidation products indicates that the polycondensation products of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride are built up essentially from phenylene-propyl units $\text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2\text{CH}_2\text{CH}_2 \text{---}$, so that the product may be termed polyphenylene-propyl. In addition to phenylene-propyl units, the main and side chains may contain elementary units of the types



containing indan residues.

In order to confirm the structure of polyphenylenepropyl based on the results of destructive oxidation, we have studied the degradation of polyphenylenepropyl by benzene in presence of aluminum chloride. It would be expected that, as in the case of polyphenyleneethyl [8], the degradation of polyphenyleneethyl would proceed as follows:



with formation of a polyphenylenepropyl of lower molecular weight. The degradation product of lowest molecular weight should be 1,3-diphenylpropane. Our experimental investigations have confirmed these suppositions; the results obtained are shown in Table 3. The low-molecular-weight degradation product that we isolated was 1,3-diphenylpropane, identified by its boiling point, specific gravity, and refractive index.

TABLE 3

Degradation of Polyphenylenepropyl by Benzene in Presence of Aluminum Chloride*
[benzene : polyphenylenepropyl = 8.8 (by weight)]

Relative amounts of aluminum chloride and polyphenylenepropyl (by weight)	Amount obtained		Mol. wt. of polyethylenepropyl
	of 1,3-diphenylpropane (% on wt. of polyphenylenepropyl)	of polyphenylenepropyl (% on original weight)	
0.8	38.0	55.4	2890
1.6	22.4	73.8	2350
2.4	22.0	58.0	2070
3.2	18.8	60.6	2050

* Mol. wt. of polyphenylenepropyl 3910; duration of reaction, 5 hours.

TABLE 4

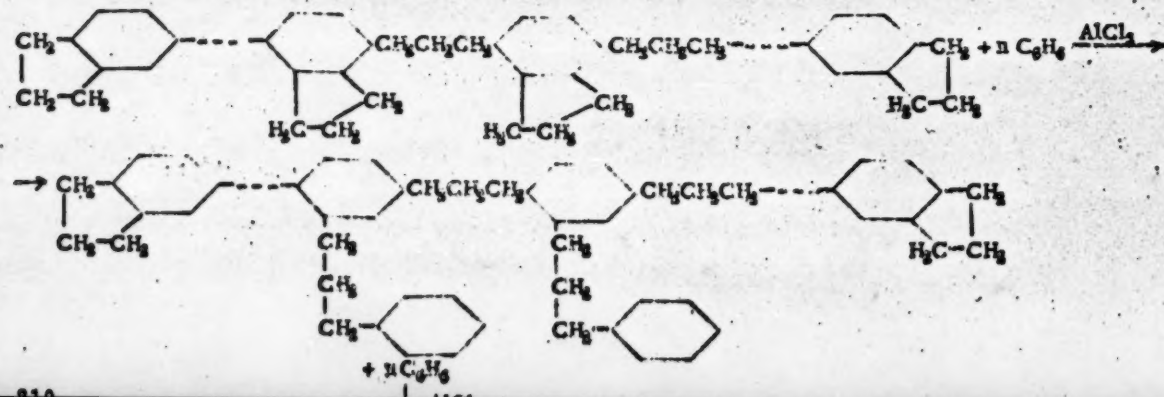
Polycondensation of 1-Bromo-3-chloropropane with Benzene in Presence of Various Catalysts

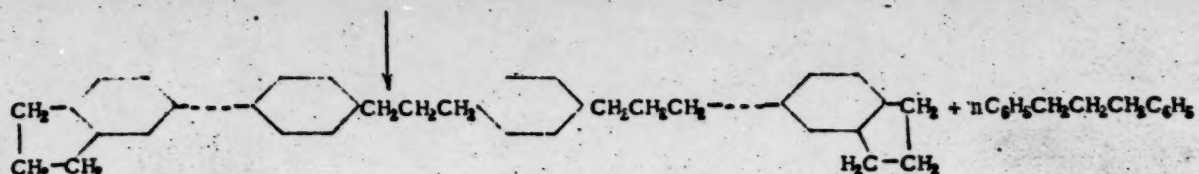
Catalyst	Yield (% of theoretical amt.)		Mol. wt. of polyphenylenepropyl
	1,3-diphenylpropane	polyphenylenepropyl	
AlCl ₃	11.0	47.3	3940
ZrCl ₄	7.7	53.5	2790
AlBr ₃	11.8	50.5	2020
FeCl ₃	12.5	13.9	1350

It will be seen from Table 3 that increase in the amount of aluminum chloride leads to decrease in the molecular weight of the polyphenylenepropyl.

This is to be explained by an increase in the number

of degradation centers with increase in the concentration of degradation catalyst (aluminum chloride). It was found at the same time that no appreciable change in the molecular weight of the polyphenylenepropyl occurs when the amount of benzene is increased at a constant polyphenylenepropyl : aluminum chloride ratio of 0.625 by weight, but the degradation product has a molecular weight of the same order as that of the original polyphenylenepropyl. As formation of 1,3-diphenylpropane (up to 29% on the weight of polyphenylenepropyl taken) is observed in this case also, absence of change in molecular weight may be explained by degradation taking place mainly in the side chains and by rupture of the saturated rings of the indan residues with formation of side chains, which then react with benzene, giving 1,3-diphenylpropane.





The degradation of 1,2,3,4-tetrahydronaphthalene rings by the action of benzene in presence of aluminum chloride, with formation of 1,4-diphenylbutane, has been previously described by us [7]. The degradation of side chains and of indan rings has no effect on the viscosimetric molecular weight, and consequently no change in this property could be observed by us.

Experiments were carried out also on the polycondensation of 1-bromo-3-chloropropane with benzene in presence not only of aluminum chloride but also of other catalysts: aluminum bromide, anhydrous zirconium chloride, and anhydrous ferric chloride. The results obtained with a benzene : 1-bromo-3-chloropropane ratio of 1.5 and 50.2 mole-% of catalyst on the amount of 1-bromo-3-chloropropane taken are given in Table 4.

It will be seen from Table 4 that the use of zirconium chloride and aluminum bromide leads to equal yields of polyphenylenepropyl, whereas, when ferric chloride is used, the yield is greatly reduced, indicating the low catalytic activity of ferric chloride in the polycondensation of 1-bromo-3-chloropropane with benzene. The molecular weight of the polyphenylenepropyl formed indicates that for this reaction the most active catalyst is aluminum chloride, and the least active is ferric chloride; zirconium chloride and aluminum bromide occupy intermediate places.

EXPERIMENTAL*

The procedure was the same as that used previously [2]. Low-molecular-weight reaction products were distilled off at 5 mm at temperatures of up to 230°. In order to purify it more completely from low-molecular-weight

TABLE 5
Effect of Catalyst Concentration on Yield and Molecular Weight of Polycondensation Products
(benzene 38 ml; 1-bromo-3-chloropropane 51.5 g)

Aluminum chloride (g)	Amount obtained		Concn. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. weight
	low-mol. wt. products (g)	polyphenylenepropyl (g)			
1.7	31.8	3.95	2.07	0.0623	1980
6.8	28.9	7.15	2.348	0.1107	3090
13.6	12.5	12.35	3.676	0.1720	3070
17.0	3.65	19.50	0.473	0.0282	3910
20.4	8.7	21.50	1.005	0.0583	3810

substances, the polyphenylenepropyl was reprecipitated from benzene solution with methanol, a 4% solution of polyphenylenepropyl in benzene being poured dropwise under stirring into six times its volume of methanol. After one day the methanolic solution was poured off, and the precipitated polyphenylenepropyl was dissolved in a small amount of benzene. The benzene solution was transferred to a dish, the benzene was evaporated off, and the polyphenylenepropyl was freed from residual benzene in a vacuum desiccator. The experimental conditions and results obtained are shown in Tables 5-8.

TABLE 6
Polycondensation of 1-Bromo-3-chloropropane with Benzene
(benzene 38 ml; aluminum chloride 20.4 g)

1-Bromo-3-chloropropane (g)	Amount obtained		Concn. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. wt.
	low-mol. wt. products (g)	polyphenylenepropyl (g)			
33.5	5.7	9.8	2.449	0.1042	2800
39.35	7.6	11.5	2.335	0.0875	2160
44.35	6.1	15.7	5.969	0.0533	3940
51.5	8.7	21.5	1.005	0.0583	3810
61.0	8.5	21.0	2.056	0.0831	2650
66.7	7.0	28.0	1.560	0.0492	2070
81.6	7.0	33.4	2.574	0.0907	2310
94.6	18.0	30.6	2.531	0.0803	2080
131.0	39.1	42.4	2.100	0.0623	1950

* Carried out with the participation of the student K.K. Shinkina.

TABLE 7
Degradation of Polyphenylenepropyl by Benzene**
(polyphenylenepropyl 5 g; benzene 50 ml)

1,3-diphenylpropane (g)	Amount obtained		Concn. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. wt.
	low-mol. wt. products (g)	polyphenylenepropyl (g)			
4	1.9	2.77	0.913	0.0402	2890
8	1.12	3.69	2.284	0.0818	2350
12	1.1	2.90	1.713	0.0540	2070
16	0.91	3.03	1.597	0.0500	2050

** Duration of reaction 5 hours; mol. wt. of polyphenylenepropyl 3910.

TABLE 8

Polycondensation of 1-Bromo-3-chloropropane with Benzene in Presence of Various Catalysts
(benzene 38 ml; 1-bromo-3-chloropropane 44.35 g)

Catalyst		Amount obtained		Concen. of benzene sol. of polyphenylenepropyl (%)	Specific viscosity	Mol. weight
Formula	Amount (g)	1,3-diphenylpropane (g)	Polyphenylenepropyl (g)			
AlCl ₃	20.4	6.06	15.71	0.969	0.0583	3940
ZrCl ₄	35.7	4.25	17.8	0.916	0.0390	2790
AlBr ₃	40.8	6.5	16.8	2.697	0.0829	2020
FeCl ₃	24.8	6.88	4.64	4.177	0.0859	1350

SUMMARY

1. The polycondensation reaction of 1-bromo-3-chloropropane with benzene in presence of aluminum chloride has been studied, and the fundamental features of the reaction have been established.
2. It has been shown that zirconium chloride, aluminum bromide, and ferric chloride are also catalysts for this reaction.
3. An explanation of the results obtained has been given.

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• See Consultants Bureau English translation, page 967.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 56. EFFECT OF STEREOCHEMICAL FACTORS ON THE POLYMERIZABILITY OF HALOGEN-SUBSTITUTED ETHYLENES

V. V. Korshak and N. G. Matveeva

The question of the effect of substituents on the ability of substituted ethylenes to undergo polymerization has attracted the attention of investigators over a long period. These investigators include Butlerov [1], Kondakov [2], Lebedev and Filonenko [3], Shorygin and Shorygina [4, 5], and other workers [6, 7]. As a result of these numerous investigations, a large amount of experimental material has been accumulated which permits an idea to be obtained of the relation existing between the structure of the substituents and the ability of substituted ethylenes to undergo polymerization [8].

One of us has shown that one of the most important factors determining the presence or absence of polymerizability in substituted ethylenes is the number and size of the substituents on the doubly bound carbon atoms [7, 8, 9, 10, 11]. In order to study this factor, we have investigated the polymerizabilities of a large number of unsaturated compounds of various structures and have obtained experimental results that fully confirm the fundamental ideas that were expressed earlier solely on the basis of the material to be found in the literature [7, 9]. In this paper we shall give the results obtained in the investigation of halogen-substituted ethylenes.

The halogen-substituted ethylenes form a class of organic compounds that has been very widely investigated from the point of view of the dependence of their polymerizability on structure. Nevertheless, in the case of a number of halogen-substituted ethylenes the presence or absence of ability to polymerize has not been established in a sufficiently reliable fashion. There are a particularly large number of desiderata of this sort among the iodine- and bromine-substituted ethylenes. We have, therefore, attempted to clear up this matter with respect to tetrachloroethylene, tetrabromoethylene, tetraiodoethylene, 1,1-dibromoethylene, and 1,1-diiodoethylene. There were no definite indications in the literature regarding the tendency of these compounds to polymerize, apart from a reference to the formation of solid substance from 1,1-dibromoethylene in presence of moist air [12]. For the purpose of this work, tetrabromoethylene, tetraiodoethylene, 1,1-dibromoethylene, and 1,1-diiodoethylene were synthesized.

Tetrabromoethylene was prepared from hexabromoethane by the splitting of bromine from the latter during distillation [13]. Tetraiodoethylene was prepared from acetylene and iodine in benzene solution [14]. 1,1-Dibromoethylene was prepared from 1,1,2-tribromoethane by the action of an alcoholic solution of caustic potash. We attempted to prepare 1,1-diiodoethylene from 1,1,1-trichloroethane by the action of aluminum iodide, but the reaction resulted in the formation of a black powder, which, on the basis of the analytical results, may be regarded as a copolymer of the following unsaturated substances: $\text{CH}_2=\text{Cl}_2$, $\text{CH}_2=\text{CCl}_2$, $\text{CH}_2=\text{CICl}$, formed by the splitting of hydrogen chloride or iodide from products formed in the reaction of 1,1,1-trichloroethane with aluminum iodide. This result gives us reason to suppose that 1,1-diiodoethylene is a polymerizable compound.

In order to determine their polymerizabilities, tetrachloroethylene, tetrabromoethylene, and tetraiodoethylene were irradiated with ultraviolet radiation (mercury lamp), for 250 hours. Other portions of these compounds were heated, with no addition and in presence of benzoyl peroxide, at 200° for 250 hours. Also, the effect of ionic catalysts was examined, the substances being subjected to the action of aluminum chloride at -60° in chloroform solution. However, none of these three compounds showed any signs of polymerization in these treatments. An attempt to induce polymerization by the use of a high pressure in which tetrachloroethylene was heated at 200° at 5000 atm. was also unsuccessful.

On the other hand, 1,1-dibromoethylene readily polymerized even during standing, and it polymerized still more readily when heated, particularly in presence of benzoyl peroxide. A solid polymer, insoluble in the usual solvents, was formed.

Thus, it was established by these experiments, that tetrachloroethylene, tetrabromoethylene, and tetraiodoethylene do not polymerize, whereas 1,1-dibromoethylene and also, evidently, 1,1-diiodoethylene, polymerize very readily.

DISCUSSION OF RESULTS

We shall now examine how the polymerizability varies in a series of halogen-substituted ethylenes according to the nature and number of the halogen atoms. For the more convenient examination of the position, we give a table showing which of the halogen-substituted ethylenes polymerize and which do not.

TABLE
Polymerizability of Halogen-substituted Ethylenes

Halogen	Internal atomic radius of the halogen (Å)	Van der Waals' atomic radius of the halogen (Å)	Polymerizing compounds	Nonpolymerizing compounds	Literature reference
I	1.33	2.1	$\text{CH}_2=\text{CHI}$ $\text{CH}_2=\text{CI}_2$		[15] —
Br	1.14	1.9	$\text{CH}_2=\text{CHBr}$ $\text{CH}_2=\text{CBr}_2$	$\text{Cl}_2=\text{Cl}_2$	[15] —
Cl	0.99	1.7	$\text{CH}_2=\text{CHCl}$ $\text{CH}_2=\text{CCl}_2$	$\text{CBr}_2=\text{CBr}_2$	[16] [17] —
F	0.64	1.4	$\text{CH}_2=\text{CHF}$ $\text{CH}_2=\text{CF}_2$ $\text{CF}_2=\text{CF}_2$	$\text{CCl}_2=\text{CCl}_2$	[18] [18] [19]
F and Cl			$\text{CF}_2=\text{CFCl}$ $\text{CF}_2=\text{CCl}_2$		[20] [21]

It is quite clear from the results given in the table that when one or two halogen atoms are present in the substituted ethylene molecule, the resulting substances are able to polymerize. One or two atoms of halogen, therefore, are not able to cause steric hindrance to polymerization. Owing to the fact that the new bond arises between two carbon atoms of which one is bound to halogen atoms and the other has only hydrogen atoms, steric factors do not play an essential part. The picture would be quite different if the polymerizing molecules became united through the carbon atoms that carried two halogen atoms. There can be no doubt that in that case considerable steric hindrance would arise from causes that will be examined in detail below, and this circumstance would make such a polymerization reaction impossible. In illustration of this question, we show some stereochemical models of 1,1-difluoro-, 1,1-dichloro-, 1,1-dibromo-, and 1,1-diiodo-ethylene, in Fig. 1.

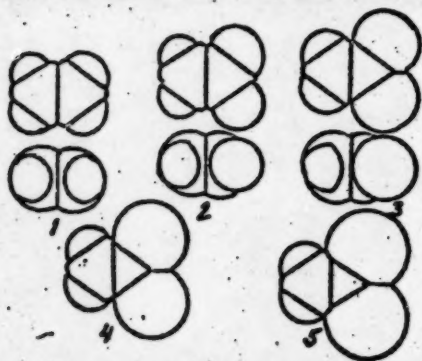


Fig. 1. Stereochemical models of the molecules of: 1) ethylene, 2) 1,1-difluoroethylene, 3) 1,1-dichloroethylene, 4) 1,1-dibromoethylene, 5) 1,1-diiodoethylene.

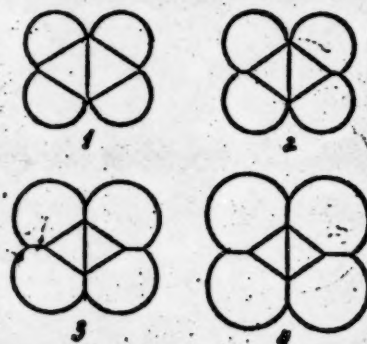


Fig. 2. Stereochemical models of the molecules of: 1) tetrafluoroethylene, 2) tetrachloroethylene, 3) tetrabromoethylene, 4) tetraiodoethylene.

We shall now examine tetrahaloethylenes. The fact that, of these compounds, only tetrafluoroethylene is able to polymerize, whereas tetrachloro-, tetrabromo-, and tetraiodo-ethylenes are not able, must be related to the sizes of the halogen atoms, for in this case there are no other essential differences between these four halogens. Evidently, the small size of the fluorine atom results in there being no steric hindrance to the polymerization of tetrafluoroethylene, and, on the other hand, the large sizes of the atoms of chlorine, bromine, and iodine are responsible for the creation of such great steric hindrance that polymerization becomes impossible. In illustration of this, stereochemical models of the molecules of these halogen derivatives are given in Fig. 2, in which the differences between them are clearly visible.

Thus, it may be concluded that when four identical substituents are present in the ethylene molecule, steric hindrance occurs only when the size of the substituent is equal to or greater than that of the chlorine atom, i.e., 1.7 Å or more. This limiting radius may be called the "limiting steric radius". It may be seen that the chlorine atom does lie on the limit by the fact that tetrachloroethylene can, under the influence of elementary fluorine, give the dimer tetrachlorodifluorobutane [22]. It is of interest to note that the Van der Waals atomic radius of the carbon atom is also equal to 1.7 Å, and we may conclude that in the case of atoms having a radius greater than that of the carbon atom, steric hindrance will arise owing to the fact that such a substituent does not allow the carbon atoms of the two uniting molecules to effect the necessary contact, which must evidently be complete. We have proposed that this effect should be called the "screening effect".

The final argument for the view that the obstacles to polymerization have a stereochemical character in the case of the tetrahaloethylenes, consists in a comparison of tetrachloroethylene with dichlorodifluoroethylene. Whereas the former does not polymerize, the latter polymerizes very readily [21]. Hence, the replacement of two large chlorine atoms by two small fluorine atoms, eliminates the screening effect and permits polymerization to occur. In illustration of this case, models of chlorotrifluoroethylene, dichlorodifluoroethylene, and 1,1-dichloroethylene are shown in Fig. 3.

EXPERIMENTAL

1,1,2-Tribromoethane

Methanol (100 ml) and caustic soda (20 g), were introduced into a three-necked flask fitted with reflux condenser, dropping funnel, and thermometer. The reflux condenser was connected to a bubbling tube, which was lowered into a 500-ml cylinder, which was one-third full of a solution of 38 ml (120 g), of bromine in carbon tetrachloride (150 ml). The flask was heated to 55-65° on a water bath, and dropwise addition of dibromoethane from the dropping funnel was commenced (109 g of dibromoethane altogether). The vinyl bromide that was evolved passed through the condenser and was absorbed in the cylinder by the bromine solution. When evolution of vinyl bromide slowed down, the bath temperature was raised to 85°, and heating was continued until evolution of gas ceased.

The solution of tribromoethane in carbon tetrachloride was washed with a sodium thiosulfate solution and then with water. It was dried over calcium chloride, and the carbon tetrachloride was then driven off. The tribromoethane (92.3 g, 48.6%) distilled over at 181-183°.

1,1-Dibromoethylene

Methanol (100 ml), caustic soda (20 g), and hydroquinone (0.5 g), were introduced into a three-necked flask fitted with reflux condenser, dropping funnel, and thermometer. The flask was warmed to 50-60° on a water bath, and 1,1,2-tribromoethane (133 g), was added gradually. When the whole of the tribromoethane had been added, the temperature was raised to 70-80° and maintained at this value for 15 minutes. The reaction mixture was then poured into water, and the oil that separated was washed with water and dried with calcium chloride. Hydroquinone was added to prevent polymerization. The 1,1-dibromoethylene (30.5 g, 33%), distilled over at 87-88°.

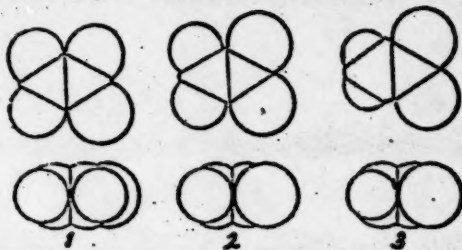


Fig. 3. Stereochemical models of the molecules of: 1) chlorotrifluoroethylene, 2) dichlorodifluoroethylene, 3) 1,1-dichloroethylene.

Polymerization of 1,1-Dibromoethylene

The polymerization of 1,1-dibromoethylene went readily when it was heated in a sealed tube, without any addition or with the addition of benzoyl peroxide. Appreciable polymer formation occurred when the monomer was stored. Poly-1,1-dibromoethylene (polyvinylidene bromide), is a white powder, insoluble in the usual solvents and decomposing at 140-150°.

Found %: C 12.97; 12.93; H 1.21; 1.18; Br 85.90; 85.85.
 $C_2H_2Br_2$. Calculated %: C 12.91 H 1.08; Br 86.00.

1,1,1-Trichloroethane

A 10% solution (25 ml) of aluminum chloride in nitrobenzene was placed in a three-necked flask fitted with reflux condenser, dropping funnel, and tube for passage of gas; 1,1-dichloroethylene (20 ml) was added, and dry hydrogen chloride was passed. Continual addition was made of 1,1-dichloroethylene, the supply being regulated so that practically no hydrogen chloride left the reaction flask [24]. When the whole (150 g) of the 1,1-dichloroethylene had been added, the reaction mixture was allowed to stand for 30 minutes, and was then poured into twice its volume of dilute hydrochloric acid. The oil was separated in a separating funnel, washed with water, and dried with calcium chloride. The 1,1,1-trichloroethane was distilled, the 72-74° fraction (89.6 g, 44.8%) being collected.

Poly-1,1-diiodoethylene (Polyvinylidene Iodide)

Carbon disulfide (100 ml), and iodine (38.5 g) were introduced into a flask fitted with reflux condenser, dropping funnel, and stirrer, and aluminum turnings (3 g) were added in small portions at a time and in such a way as to prevent any considerable rise in temperature. When the whole of the aluminum had dissolved, 1,1,1-trichloroethane (15 g) was added slowly, when the temperature of the reaction mixture rose and it was necessary to cool the flask. When addition of 1,1,1-trichloroethane was complete, stirring was continued for one hour, and the reaction mixture was then poured into dilute hydrochloric acid. The precipitate was filtered off, washed with alcohol, and dried (20.8 g, 61.1%). Polyvinylidene chloride is a black powder, insoluble in the usual solvents; it decomposes when heated.

Hexabromoethane

Hexachloroethane (20 g), and bromine (80 g) were placed in a test tube. Aluminum (4.6 g), first in small pieces and later in large pieces, was stirred into the mixture. At first the reaction was very vigorous: the aluminum floated up to the surface and burst into flame, so that it was necessary to wait until one portion of aluminum had reacted before adding the next. When the whole of the aluminum had reacted, the reaction mixture was poured into dilute hydrochloric acid, and the precipitate that formed was filtered off [23]. Unchanged bromine was removed from the hexabromoethane by washing with dilute alkali and then several times with water. Recrystallization from alcohol yielded hexabromoethane (35.3 g, 76.95%); it decomposes without melting at 200-210°.

Tetrabromoethylene

Hexabromoethane (20 g) was distilled at 180-200° from a Wurtz flask. The mixture of tetrabromoethylene and bromine was collected in a beaker containing caustic potash solution, and the precipitate that formed was filtered off, washed with water, and dried in the air. The dry product was distilled again into a beaker containing alkali, and the precipitate was washed with water, dried, and crystallized from alcohol [13]. The tetrabromoethylene (10.2 g, 74.7%) was formed in glistening plates, m.p. 50-51°.

Tetraiodoethylene

Finely crushed calcium carbide (50 g), and iodine (200 g) were placed in a porcelain beaker, capacity 250-300 ml, and benzene (100 ml) was added under stirring. A stream of nitrogen was passed through a tube that did not reach to the surface of the liquid, and water (120 ml) was added, the temperature being maintained not above 45°. When the whole of the water had been added, stirring was continued for a further one hour. The precipitate was then allowed to settle, and the liquid was carefully poured off. The benzene layer was separated and the benzene was removed, the flask being heated under vacuum on a water bath. The calcium hydroxide settlements were treated several times with dichloroethane at 60-70°, and when the solution was cooled, crystalline tetraiodoethylene separated and was added to the portion obtained from the benzene layer; the mixed sample was recrystallized from dichloroethane [14]. Tetraiodoethylene (69 g, 18%) was obtained in the form of yellow

plates, melting with decomposition at 192-193°; it is of very good solubility in carbon disulfide, of good solubility in hot dichloroethane, benzene, and acetic acid, and insoluble in water.

SUMMARY

1. Polymerizability has been investigated in the halogen-substituted ethylene series, tetra- and dihaloethylenes being taken as examples.
2. It has been established that steric hindrance to polymerization in the substituted-ethylene series is determined by the number and sizes of the substituents on the doubly bound carbon atoms.
3. It has been found that the "limiting steric radius" for a substituent, is about 1.4-1.7 Å in the case of tetra-substituted ethylenes.
4. It has been shown that in the case of the asymmetrical dihaloethylenes polymerization is possible whatever the halogen may be.
5. The polymerization of 1,1-dibromoethylene has been investigated.
6. It has been shown that tetrabromo-, tetrachloro-, and tetraiodoethylenes are not able to polymerize.

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COMMUNICATION I. CATALYTIC POLYMERIZATION OF STYRENE IN PRESENCE OF
FERRIC CHLORIDE AND OF STANNIC CHLORIDE

319

This complex acts as catalyst in the polymerization [7].

The mechanism of the action of stannic chloride, as described by Williams [8] and Gantmakher and Medvedev [9], is based on the same hypothesis. A number of metal chlorides have a chlorinating action [8] (for example, antimony pentachloride), and this complicates the course of the reaction: in polymerization processes, in addition to the polymer, the dichloride $C_6H_4Cl_2$ is formed in an amount that corresponds to half of the amount of added catalyst.

It is doubtful whether it is possible to extend the mechanisms discussed above to all metal chlorides: further detailed and more precise investigation is necessary. Also, generalizations cannot be so readily made about the chemical properties of the chlorides themselves on the basis only of the fact that they can induce polymerization processes, for these processes are extremely sensitive to slight traces of substances having oxidation-reduction properties. It is well known that metal chlorides vary greatly in their oxidation-reduction potentials.

These considerations prompted us to carry out a comparative assessment of the action of metal chlorides on unsaturated compounds in presence and in absence of oxygen. Investigations in this direction showed that ferric chloride acted as a catalyst for the polymerization of styrene only in presence of air. An attempt to effect this process in an atmosphere of nitrogen led to negative results. Stannic chloride, however, brought about polymerization processes both in presence and in absence of oxygen.

Analysis of the polymer obtained in the earlier experiments on the polymerization of styrene under the influence of ferric chloride in an atmosphere of air showed that the product contained a considerable amount of oxygen (16-17%). This suggested to us that the product was a polymeric peroxide, similar to those obtained by Barnes and coworkers [10] by the action of oxygen on styrene. It was found later, however, that when the polymer was submitted to repeated reprecipitation its oxygen content fell (see table). The polymer, after being reprecipitated three times, analyzed as follows: C-91.15%; H-8.26% (total 99.35%), and was therefore a practically pure hydrocarbon. The oxygen found in the first analyses did not therefore enter into the constitution of the polymer molecule.

The solvent from which the reprecipitation of the polymer had been carried out was carefully fractionated, and it was found possible to isolate a liquid of b.p. 179° having the characteristic odor of benzaldehyde. The substance was very readily oxidized in the air, giving, as analysis showed, benzoic acid. Thus, in addition to the polymer, benzaldehyde was formed in fairly large amount (8-10 g) in every experiment. The possibility was not excluded that the benzaldehyde was contaminated with benzoic acid, for analysis gave a somewhat exalted oxygen content. The benzaldehyde remained liquid, however, when kept in sealed tubes, no separation of benzoic acid crystals being observed, and the amount of contamination by the acid must have been very slight. Benzoic acid might have been present also in the resin left after removal of solvent and benzaldehyde by distillation, but no acid was isolated from the resin.

Staudinger [11] remarked that the products of the polymerization of styrene in presence of oxygen always contain traces of benzaldehyde. Stobbe [12] also found that when styrene is subjected to the action of light in presence of oxygen, both polymer and benzaldehyde are formed.

As already indicated, an attempt to polymerize styrene in presence of ferric chloride in an atmosphere of nitrogen led to negative results. Also, as it was desired to learn more about the part played by ferric chloride as a catalyst, control experiments were carried out in which styrene was subjected to the action of air in absence of catalyst; conditions of time and temperature were the same as those for the experiments with ferric chloride and access of air. Polymerization did not occur. Fractional distillation of the products obtained in the control experiments and also in the experiments carried out in presence of ferric chloride in a nitrogen atmosphere yielded styrene quantitatively; no benzaldehyde was detected.

It was therefore shown that for polymerization of styrene to occur under our experimental conditions (comparatively short time and without heat) both oxygen and ferric chloride must be present. On the basis of these facts it may be assumed that ferric chloride catalyzes the oxidation of styrene by air, and the peroxide compounds so formed bring

about the polymerization of styrene. The presence in our experiments of an appreciable amount of benzaldehyde, formed evidently by the oxidation of styrene, may also play a significant part in the polymerization of styrene in air under the influence of ferric chloride. It is well known that benzaldehyde that has not been specially purified is readily oxidized. It is possible that the oxidation of the aldehyde is a catalytic process occurring only in presence of traces of heavy metals, mainly iron: completely pure benzaldehyde does not oxidize. Rikhe [13] has pointed out that the oxidation of aldehydes proceeds readily in presence of a small amount of an iron salt. It is possible that the ferric chloride present in our experiments catalyzed the oxidation of benzaldehyde. The monoxide formed by the oxidation of the benzaldehyde would rapidly decompose, yielding, in addition to benzoic acid, oxygen in an active form, which would bring about the polymerization of the styrene.

Observations on the variation of the refractive index during the polymerization of styrene in presence of ferric chloride indicated that there was a considerable period of induction. This delay in the onset of the polymerization process may be explained on the hypothesis that at first oxidation processes occurred, and these then brought about the polymerization processes.

As indicated above, polymerization of styrene in presence of stannic chloride evidently proceeds by a completely different mechanism. Polymerization occurred in our experiments both when air was present and when an atmosphere of nitrogen was used. In both cases analysis indicated that the same product had been formed. In all the experiments the onset of polymerization was preceded by a short period of inhibition (10-15 minutes), which may be explained by the presence of hydrogen chloride in the catalyst [8]. In the course of the reprecipitation of the polymers, no side products were detected.

The mechanism of the action of stannic chloride, as we have already noted, has been described in the papers of Williams [8] and Gantmakher and Medvedev [9]. It may be supposed also that stannic chloride, owing to its oxidation-reduction properties, effects polymerization processes both in presence and in absence of oxygen, but this supposition requires further investigation.

EXPERIMENTAL

TABLE

Composition of Polymer Before and After Purification

Polymer	Analysis		Calc. for $(C_8H_8)_n$
	C (%)	H (%)	
Before reprecipitation	85.60	7.35	% C 92.3 % H 7.7
After the 1st reprecipitation	90.16	7.78	
After the 3rd reprecipitation	91.15	8.20	

1. Starting Substances. Freshly distilled styrene was used, distillation being carried out under reduced pressure in an atmosphere of nitrogen. The styrene taken for reaction had the following constants: b.p. 72° at 30 mm; n_D^{20} 1.5460, d_4^{20} 0.9065. The catalysts used were: a 5% solution of $FeCl_3 \cdot 6H_2O$ in absolute butyl alcohol, and $SnCl_4$. The stannic chloride was purified by repeated vacuum distillation.

2. Polymerization of Styrene in an Atmosphere of Air in Presence of Ferric Chloride.

The following experiment is typical of the series. It was carried out at room temperature (19-20°) in a three-necked flask fitted with mechanical stirrer, reflux condenser, and thermometer. Styrene (104 g) was poured into the flask, and the catalyst (0.24 g of a 5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol) was introduced. Every day at 10 a.m., the refractive index of the mixture was checked, and a further 0.04 g of catalyst was then added. For the first two days of the experiment the refractive index remained unchanged, but, beginning from the third day, it gradually rose. After fourteen days the material, which had become appreciably thicker, was poured into a porcelain dish and left in the air. On the next day the polymer had become solid. The polymer obtained (98 g before reprecipitation) was dissolved in benzene and precipitated from solution with ethanol, after which it was exposed to a vacuum for some time. The reprecipitation was repeated three times, and after each treatment the polymer was analyzed (see the table). The weight of reprecipitated polymer was 86.2 g (82.2%); it had a molecular weight of 5688* and a viscosity of 1.169 centipoise.

Found %: C 91.15, 91.25; H 8.20, 7.86
 $(C_8H_8)_n$ Calculated %: C 92.3; H 7.7

* In all experiments the viscosity of a solution of 1 g of polymer in 100 ml of benzene was determined at 20° in an Ostwald viscosimeter; the molecular weight was determined cryoscopically in benzene.

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* See Consultants Bureau English translation, page 643 ff.

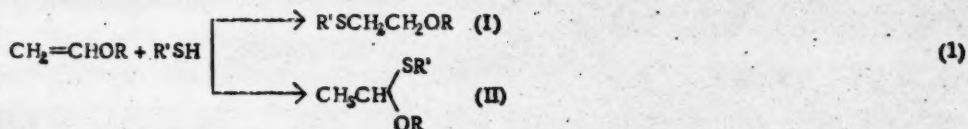
COMMUNICATION 6. REACTIONS OF THIOLS WITH VINYL ETHERS

M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

The addition in accordance with Markovnikov's rule of a number of substances to vinyl ethers evidently has an ionic mechanism; it has been studied in some detail by one of us and coworkers [1]. On the other hand very little is known about the reactions of vinyl ethers that may be interpreted as being of the free-radical type. Thus, there are data about copolymerization reactions of alkyl vinyl ethers with other substances in presence of peroxides [2], and also about the addition of carbon tetrachloride to butyl vinyl ether in presence of benzoyl peroxide [3]. Finally, the partially "abnormal" addition to certain vinyl ethers of hydrogen sulfide and of the alkoxyethyl thiols formed has been the subject of some of our previous communications [4a, 4b, 4c]. The reaction was carried out in presence of small amounts of hydrogen chloride as catalyst in dioxane.

In this connection, it was considered to be of interest to study the products of the reaction of vinyl ethers with thiols, since the particular tendency of the latter to undergo "abnormal" addition of the free-radical type is generally known [5]. This has been carried out in the present investigation, ethyl vinyl and butyl vinyl ethers being taken as examples. As thiols, the following were taken: ethanethiol, 1- and 2-alkoxyethanethiols, and (in one case) thioacetic acid.

The results obtained indicate that the reaction is a very peculiar one, not only the "abnormal" product, which is always obtained when thiols react with olefins [5], being formed. The product is a mixture of a diether of 2-mercaptoethanol (I) (the "abnormal" product) and a monothioacetal (II) (the "normal" product), the former predominating:



The composition of the mixture depends both on the nature of the ether taken and also on the nature of the thiol (see Table 1). Ethyl vinyl ether reacts with a greater velocity than butyl vinyl ether, and it gives a greater yield of "abnormal" products. Among the thiols, the highest percentage of "abnormal" addition is given by those that are more easily oxidized (1-alkoxyethanethiols, thioacetic acid). The more stable thiols (ethanethiol, 2-alkoxyethanethiols) form up to 40% of "normal" products with butyl vinyl ether, although the reaction is in this case very slow at room temperature and may be brought to completion only by the application of heat.

A completely unexpected effect was shown on this reaction by the substances formed when vinyl ethers or thiols are allowed to stand in the air. These "peroxide" compounds (at least in the case of ethyl vinyl ether and ethanethiol) have no catalytic effect on the abnormal reaction; on the contrary, they retard it. As a result, the composition of the products and the rate of reaction depend greatly on the way in which the starting materials are purified (see Table 4), though in a sense that is the reverse of that required by Kharash's peroxide theory [6].

We have established also that when freshly distilled vinyl ether and thiol, not containing peroxides, are introduced into an ampoule, which is evacuated under cooling and then sealed, then, whatever the structures of the substances may be, slow formation occurs of the abnormal product only, namely, the diether of

* The only similar fact that we have found in the literature is the observation of Hoog and Eichwald that a mixture of heptane and 1-octene that has been kept in the air for a long period and contains peroxides unites with mercaptoacetic acid more slowly than a freshly prepared mixture does [7]. The authors do not indicate the direction of the addition.

TABLE 1

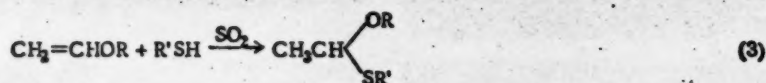
Products Formed by Reaction of Freshly Distilled Vinyl Ethers with Thiols in Presence of Air (Equation 1)

Vinyl ether	Thiol	Composition of reaction products (%)	
		(I)	(II)
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{SH}$	92-97	8-3
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	$\text{CH}_3\text{CH}(\text{SH})\text{OC}_2\text{H}_5$	100	—
$\text{CH}_2=\text{CHOC}_4\text{H}_9$	$\text{C}_2\text{H}_5\text{SH}$	60-70	40-30
$\text{CH}_2=\text{CHOC}_4\text{H}_9$	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{SH}^{**}$	60-65	30-35
$\text{CH}_2=\text{CHOC}_4\text{H}_9$	$\text{CH}_3\text{CH}(\text{SH})\text{OC}_4\text{H}_9$	90-91	10-9
$\text{CH}_2=\text{CHOC}_4\text{H}_9$	CH_3COSH	100	—

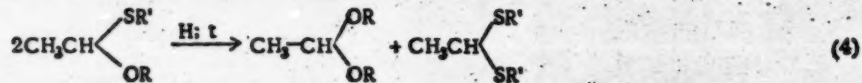
is probably to be found in the fact that the thiol group scarcely forms hydrogen bonds with other substances, while at the same time hydrogen bonds are essential (according to the hypothesis advanced by one of us [1]) for the formation of the complexes that are precursors in an ionic reaction. Introduction of the very slightest amount of a suitable catalyst of an acidic character induces rapid addition reaction of the thiol in accord with Markovnikov's rule. For this purpose we have made use of very small amounts of sulfur dioxide, by the aid of which we have previously brought about the addition of hydrogen sulfide to vinyl ethers [9]. It is possible that

sulfur dioxide forms compounds of the type $\text{O}=\text{S} \begin{matrix} \text{OH} \\ \text{SR} \end{matrix}$, with thiols, and these products act as acidic catalysts

in this addition reaction (Equation 3):



In the reactions of ethanethiol with ethyl vinyl and butyl vinyl ethers, the yield of the monothioacetal, which under these conditions is the sole product (Equation 3), attains 80-85%*. Under our conditions there were practically no side products, although we have shown previously [4], taking β -alkoxy-substituted monothioacetals as examples, that these compounds are unstable and tend to undergo a disproportionation reaction:

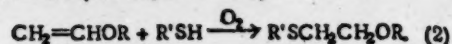


The catalytic addition of thiols to vinyl ethers in accord with Markovnikov's rule proceeds, therefore, very readily, and does not demand the severe conditions required in the analogous reaction with alkenes [11,12,13].

* A number of publications have been published recently on the addition of thiols to vinyl ethers in presence of α -chloro ethers, *p*-toluenesulfonic acid, and sulfonyl chloride, but the use of these catalysts leads to yields of monothioacetals of not more than 40-45% and to the formation of a large amount of mercaptals as secondary products.

** Unlike the other thiols, for which the reaction was carried out at room temperature, 2-butoxyethanethiols was caused to react at 60-70°.

2-mercaptoethanol (Equation 2). When the mixture is heated at 60-70°, a quantitative yield of this product can be readily obtained (see Experimental):

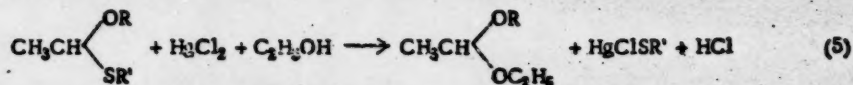


We consider that the reaction is catalyzed by traces of oxygen that remain, under these conditions, in the liquid and on the walls of the ampoule. We have thus obtained also a second unexpected result: the presence of oxygen in large amounts (when the reaction is carried out in air) causes a general acceleration of the reaction, but, at the same time, formation of "normal" addition products.

The noncatalyzed addition of thiols to alkyl vinyl ethers in accord with Markovnikov's rule is, according to our experimental results, extremely slow under all conditions. The cause of this

Thus, in the present investigation we have worked out the conditions for the synthesis from vinyl ethers of two series of compounds that have practically not been described previously, the yields being almost quantitative; these compounds are monothioacetals and diethers of 2-mercaptoethanol.

The identification of these sulfides, and also the analyses of mixtures of isomeric products, was based on the differing behaviors of these two types of compounds toward an alcoholic solution of mercuric chloride. Monothioacetals are quantitatively split by this reagent, as also are other representatives of this series that we have previously prepared from vinyl ethers [4a, 4, 4c] (Equation 5):



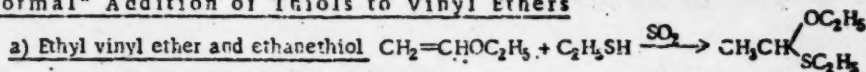
Diethers of 2-mercaptoethanol give the complex salts usually formed by sulfides under these conditions. The compositions of the mixtures were therefore determined by the previously described method [4a] by titration with a standard alkali solution after treatment of a weighed sample of the material with an excess of an alcoholic solution of mercuric chloride.

As pointed out above, a number of the regular features that we have discovered in the addition of thiols to vinyl ethers cannot be reconciled with the usual ideas of Kharash's "peroxide" theory. A theoretical treatment of these phenomena will be given on the basis of further supplementary experimental data.

EXPERIMENTAL

In all experiments an excess of the vinyl ether was used: this permitted the end of the reaction to be judged approximately by the disappearance of the thiol odor. All the yields are calculated on the amount of thiol taken for reaction. In most of the experiments, the vinyl ethers were purified by the method employed in the Vinyl Compound Laboratory [14], but, in view of the particular sensitivity of the reactions studied with respect to air oxidation of the vinyl ethers, all the operations of purification and drying were done as quickly as possible. The ether, after being washed with water, was dried for 1-2 days over potassium carbonate, distilled, kept for 1-2 days over sodium, and redistilled just before the experiment. The ether so obtained gave a practically negative test for peroxide with thiocyanate. The thiols were also freshly distilled for use. The method of titrating mixtures of isomeric sulfides has been previously described by us in detail [4a].

I. "Normal" Addition of Thiols to Vinyl Ethers



A slow stream of dry sulfur dioxide gas was passed for three minutes through a mixture (previously cooled to -20° in a stream of nitrogen) of ethanethiol (3.9 g) and ethyl vinyl ether (7.2 g) contained in a flask provided with stirrer. The cooling mixture was removed, and the temperature rapidly rose to $+30^\circ$; the mixture was then again cooled to $+15-20^\circ$. Stirring was continued at this temperature for a further two hours, and the mixture was then left overnight. The reaction product was vacuum-distilled: the excess ethyl vinyl ether was collected in a cooled trap, and the residue yielded a substance (6.7 g, 81.7%) of b.p. $53-54^\circ/31$ mm, n_D^{20} 1.4428.

1-Ethoxy-1-(ethylthio)ethane has b.p. $67.5-68.5^\circ$ at 50 mm; n_D^{20} 1.4428; d_4^{20} 0.9000; found MR 39.51; calculated MR 39.52.

Found %: C 53.64; 53.74; H 10.57; 10.50; S 23.54; 23.69
C₆H₁₄OS. Calculated %: C 53.68; H 10.51; S 23.89

1-Ethoxy-1-(ethylthio)ethane has a sweetish ethereal odor, which turns rapidly after inhalation into the odor of ethanethiol.

* The synthesis of this substance from ethyl vinyl ether and ethanethiol in presence of SOCl_2 was described by Kipris, Soloway, and Ornfelt [10] when the greater part of the present investigation had been completed. These authors, however, obtained a low yield (40%) of the product, which, moreover, they characterized only by the boiling point ($33-35^\circ/5$ mm) and analysis for C and H.

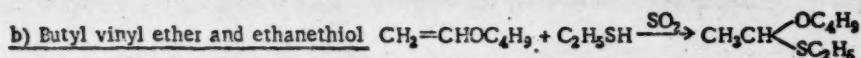
The action of an alcoholic solution of mercuric chloride resulted in the quantitative precipitation of ethylthiomercury chloride and the formation of HCl (Equation 4). Titration with standard alkali after the treatment with excess of the alcoholic solution accounted for 96.9% of the theoretical amount of HCl. The substance (0.59 g) with mercuric chloride (1.2 g, as a 20% solution in alcohol) quickly gave a white finely crystalline precipitate, which, after being washed on the filter with dry ether and then dried, weighed 1.40 g (theoretical amount: 1.38 g). This substance did not dissolve in boiling alcohol or ether, and did not melt, but blackened at 350-360°; these properties correspond to those described in the literature [15] for ethylthiomercury chloride.

Found %: S 10.57; 10.50
 C_2H_5SHgCl . Calculated %: S 10.82

TABLE 2

Conditions of "Abnormal" Addition of Ethanethiol to Ethyl Vinyl Ether

Expt. No.	Amount taken (g)		Duration of reaction (days)	Temperature of reaction	Properties of reaction products			Yield of reaction products (%)
	thiol	ether			B.p. (°C)	Pressure (mm Hg)	n_D^{25}	
6	6.3	15.0	7	Room	—	—	1.4507	3
8	6.9	16.0	60	Room	76-77	34	1.4507	77.0
15	6.0	15.0	7	Room, apart from 60 hrs at 60°	83.5-84.5	48	1.4508	93.1



Ethanethiol (6.8 g) and butyl vinyl ether (15 g) were each distilled in a stream of nitrogen, and were then mixed and cooled by liquid nitrogen in an ampoule having two side tubes. A slow stream of sulfur dioxide was passed through the ampoule for three minutes, and the ampoule, while still being cooled, was connected to an oil pump. After 30 minutes it was sealed off under a residual pressure of 4 mm. The ampoule was set aside at room temperature for 20 hours and then opened. No unchanged ethanethiol was found. The excess of butyl vinyl ether (3.6 g) was distilled off under reduced pressure, and the following fractions were then obtained:

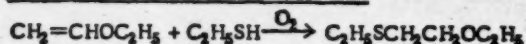
Fraction I, b.p. 36-51° at 4 mm, 1.0 g; n_D^{20} 1.4448

Fraction II, b.p. 49-51° at 3-4 mm, 15.5 g; n_D^{20} 1.4468

A small resinified residue (0.9 g) remained in the flask. Fraction II was practically pure 1-butoxy-1-(ethylthio)ethane obtained in 86.5% yield. Titration with standard alkali after addition of excess of a 20% alcoholic solution of mercuric chloride accounted for 93.5% of the theoretical amount of HCl. After repeated fractionation the substance had b.p. 56-57° at 5 mm; n_D^{20} 1.4461; d_4^{20} 0.8855; found MR 48.76; calculated MR 48.76. A more detailed characterization of this substance is given below, where reference is made to its isolation by fractionation through an efficient column of a mixture of "normal" and "abnormal" products obtained by addition of ethanethiol to butyl vinyl ether in the air.

II. "Abnormal" Addition of Thiols to Vinyl Ethers

a) Ethyl vinyl ether and ethanethiol



All the experiments were carried out in an apparatus consisting of three ampoules connected together by a glass four-way piece, one end of which ended in a tap. Two of the ampoules were provided with side tubes having ground stoppers, and the third had a capillary constriction. Freshly distilled ethanethiol and freshly distilled ethyl vinyl ether were respectively introduced into the first two ampoules. The tap was in the closed position, and the

two ampoules were cooled by immersion in liquid nitrogen. The apparatus was then connected to a vacuum pump through the tap and was evacuated for 30 minutes to a residual pressure of 3-4 mm. The tap was then closed, the ampoules containing the substances were taken out of the cooling mixture, and their contents were distilled, under the reduced pressure, into the third ampoule (with the constriction), which was immersed for this purpose in liquid nitrogen. When the distillation was complete, the apparatus was again connected to the vacuum pump, and the ampoule was fused off at a residual pressure of 3 mm. When the ampoule was opened, unchanged vinyl ether and thiol were distilled under reduced pressure into a well cooled trap. The residue was distilled at 35-50 mm.

It will be seen from Table 2 that reaction is not complete at room temperature even after two months. When the mixture was heated to 60-65°, a good yield of 1-ethoxy-2-(ethylthio)ethane—the only reaction product—was obtained in seven days, in the course of which heat was applied for a total period of 60 hours.

1-Ethoxy-2-(ethylthio)ethane has b.p. 78-78.5° at 35 mm; n_D^{20} 1.4507; d_4^{20} 0.9126; found MR 39.57; calculated MR 39.52.

Found %: C 53.54; 53.76; H 10.54; 10.55; S 23.95; 24.17
 $C_6H_{14}OS$. Calculated %: C 53.68; H 10.51; S 23.89

TABLE 3

Conditions of "Abnormal" Addition of Ethanethiol to Butyl Vinyl Ether

Expt. No.	Amount taken (g)		Duration of reaction (days)	Period of heating at 60° (hr)	Properties of reaction products			Yield of reaction products (%)
	thiol	ether			B.p. (°C)	Pressure (mm Hg)	n_D^{20}	
5 a)	9.0	19.5	3	12	65-66.5	4.5	1.4521	44.9
8 a)	5.6	15.0	7	35	65-66	5	1.4520	47.9
7 b)	5.2	15.2	6	35	62-63	4	1.4520	96.8
3 a)	6.8	15.0	40	Not heated	86.5	11	1.4520	78.1

a) Carried out in the three-ampoule apparatus.

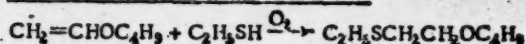
b) Carried out in an ampoule having a constriction.

1-Ethoxy-2-(ethylthio)ethane is a colorless liquid of sweetish odor—somewhat more pleasant than that of the isomeric monothioacetal. With mercuric chloride in alcoholic solution it forms a viscous liquid complex compound, the composition of which was not investigated, and in the course of the reaction the medium remains neutral to Methyl Orange.

It is oxidized very vigorously by hydrogen peroxide in acetic acid with formation of the corresponding sulfoxide; when 1-ethoxy-2-(ethylthio)ethane (10 g) was oxidized with a solution of 29.6% H_2O_2 (9 ml) in glacial acetic acid (16 ml), the product was a substance (the sulfoxide; 5.7 g, 50.7%) having b.p. 112.2-113.5° at 6 mm; n_D^{20} 1.4696; d_4^{20} 1.0354; found M (cryoscopically in benzene) 145.5; 147.5; calculated M 150.2; found MR 40.45; calculated MR 40.14.

Found %: C 48.29; 48.09; H 9.45; 9.65; S 21.44; 21.69
 $C_6H_{14}O_2S$. Calculated %: C 47.96; H 9.39; S 21.30

b) Butyl vinyl ether and ethanethiol



The reaction between butyl vinyl ether and ethanethiol, under the conditions described above for ethyl vinyl ether, proceeds more slowly and requires a longer period of heating (see Table 3). The reaction is effected somewhat more rapidly by introducing the two reactants not into the above-described apparatus, but into an ampoule having

a capillary constriction, which is then cooled, evacuated to a residual pressure of 3-4 mm, and sealed off. Under these conditions, evidently, a somewhat greater amount of oxygen remains dissolved in the reaction mixture. The reaction conditions will be clear from Table 3.

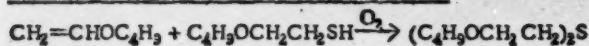
The only reaction product obtained in all of the experiments was 1-butoxy-2-(ethylthio)ethane, b.p. 65-66° at 5 mm; n_D^{20} 1.4520; d_4^{20} 0.8979; found MR 48.77; calculated MR 48.76 (for a more detailed characterization see below, where a description is given of the isolation of this substance by fractionation through a column of the reaction mixture obtained by the action of ethanethiol on butyl vinyl ether in presence of air). In its properties the substance is reminiscent of 1-ethoxy-2-(ethylthio)ethane.

With mercuric chloride, 1-butoxy-2-(ethylthio)ethane gives a liquid complex compound, and the medium remains neutral during the reaction. 1-Butoxy-2-(ethylthio)ethane (21.5 g) was oxidized in glacial acetic acid (25 ml) with 27.6% H_2O_2 (16.5 ml) and gave the corresponding sulfoxide (18.3 g, 72.3%), b.p. 112-112.5° at 15 mm; 117.2-117.4° at 3 mm; n_D^{20} 1.4664, d_4^{20} 0.9955; found MR 49.64; calculated MR 49.38.

Found %: C 53.92; 53.98; H 10.23; 10.26; S 17.81; 17.69

$C_8H_{18}SO_2$. Calculated %: C 53.89; H 10.17; S 17.99

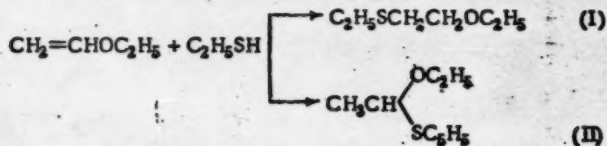
c) Butyl vinyl ether and 2-butoxyethanethiol



Freshly distilled 2-butoxyethanethiol (6 g) of b.p. 47-48° at 5 mm and n_D^{20} 1.4489 [4a] and butyl vinyl ether (15 g) were frozen by liquid nitrogen in an ampoule having a capillary constriction. The ampoule was evacuated to a residual pressure of 5-7 mm and sealed off. Heating at 60-65° was at intervals for a total time of 50 hours in the course of seven days. When the ampoule was opened, no unchanged thiol could be detected. The excess (10 g) of butyl vinyl ether was distilled off, and the residue distilled over completely at 130-131° / 4.5 mm (9.4 g, 93.9%; n_D^{20} 1.4560). It did not give a red coloration with Methyl Orange after the addition of mercuric chloride in ethanol. In its properties it corresponded exactly to the previously described bis(2-butoxyethyl) sulfide [4a, 4b].

III. Addition of Thiols to Vinyl Ethers in Presence of Air and of the Oxidation Products of the Starting Materials

a) Ethyl vinyl ether and ethanethiol



A weighed amount of ethyl vinyl ether was mixed with a weighed amount of ethanethiol in a small flask having a ground stopper, and the mixture was allowed to stand at room temperature. Unchanged starting materials were distilled off at 45-50 mm and were retained by a well cooled trap. The residue was distilled from a flask through a fractionating column. The mixture of ethoxy(ethylthio)ethanes was analyzed by titration with alkali after addition of excess of mercuric chloride as a 20% solution in ethanol. The yields, compositions, and constants of the mixtures of sulfides obtained under various conditions with respect to the purification of the starting materials are given in Table 4.

The results given in Table 4 show that freshly purified ethanethiol and ethyl vinyl ether react in presence of air at room temperature appreciably more rapidly than in an evacuated vessel, and they give the "abnormal" product almost exclusively (Experiment 12). Ethyl vinyl ether that has been subjected to the action of the air and contains peroxides unites more slowly with the thiol with formation of a greater amount of "normal" product (Experiments 13, 14 and 16).

Oxidation of the thiol by long storage leads to the same result (Experiment 11). The constants of the mixtures of sulfides (boiling points and refractive indices) correspond, as will be seen from Table 4, to their compositions, as determined by titration. Thus, the products formed by the air-oxidation of vinyl ethers and thiols do not catalyze the addition reaction proceeding contrary to Markovnikov's rule, but retard it.

TABLE 4

Products of the Addition of Ethanethiol to Ethyl Vinyl Ether in Presence of Air

Expt. No.	Amt. taken (g)		Purification of starting materials	Duration of reaction (days)	Properties of reaction products			Yield (%)	Composition (%)	
	thiol	ether			B.p. (°C)	Pressure (mm Hg)	n_D^{20}		(I)	(II)
12	6.0	15.0	a	7	82-84	47	1.4506	94.6	97.5	2.5
14	6.2	15.0	b	10	82-86	53	1.4502	89.5	90.5	9.5
11	6.2	15.0	c	7	77-84	48	1.4486	78.2	69.5	30.5
16	10.2	25.0	d	6	68-84	53	1.4465	13.3	34.5	65.5
13	5.6	15.0	d	12	75-86	53	1.4495	73.5	78.4	21.6

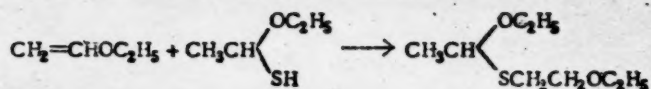
a) The ethyl vinyl ether was washed five times with water and dried with potassium carbonate and sodium. It was distilled twice over sodium before the actual experiment. It gave negative results in the thiocyanate test for presence of peroxides. The ethanethiol was dried over Na_2SO_4 and distilled twice in a stream of nitrogen before the actual experiment (b.p. 35.5-36°).

b) The ethyl vinyl ether, after being washed, was preserved for a month over sodium. It was distilled before the experiment. The thiol was purified as in Expt. 12.

c) The ethyl vinyl ether was purified as in Expt. 12. The ethanethiol was distilled and then preserved in sealed ampoule (in presence of air) for six months. It was not redistilled before the experiment.

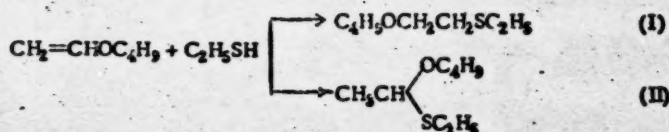
d) The ethyl vinyl ether was purified as in Expt. 12 and then left in the air for two weeks. It gave a definite reaction for peroxides. Thiol purified as in Expt. 12 was added to it.

b) Ethyl vinyl ether and 1-ethoxyethanethiol



Freshly distilled ethyl vinyl ether (11 g) was added to freshly distilled 1-ethoxyethanethiol (8 g) having b.p. 38-39° at 65 mm and n_D^{20} 1.4378 [8]. After a week the reaction mixture was diluted with an equal amount of ether, washed five times with 5% aqueous KOH and with water, dried, and distilled. The excess of ethyl vinyl ether was distilled off, and further distillation yielded a sulfide (10.8 g, 79.8%) having the properties of 1-ethoxyethyl 2-ethoxyethyl sulfide, which we have described previously [4a]: b.p. 65-68° at 3.5 mm; n_D^{20} 1.4505. Titration with alkali after addition of mercuric chloride indicated a 97.7% content of this sulfide in the fraction described. In the air, 1-ethoxyethanethiol adds to ethyl vinyl ether practically completely in the direction that is contrary to Markovnikov's rule.

c) Butyl vinyl ether and ethanethiol



Butyl vinyl ether unites with ethanethiol in presence of air appreciably more slowly than ethyl vinyl ether, and the reaction cannot be brought to completion without warming (see Table 5). Even freshly distilled materials react with formation of large amounts of the monothioacetal (II) — the addition product corresponding to Markovnikov's rule.

Experiment 2. Freshly distilled ethanethiol (25 g) was mixed in a flask with freshly distilled butyl vinyl ether (60 g), which was purified extremely carefully. The mixture was heated in a sealed ampoule (in presence of air; without evacuation) for 12 hours in a boiling water bath. After two weeks, the excess butyl vinyl ether and

TABLE 5

Reaction between Butyl-Vinyl Ether and Ethanethiol in Presence of Air

Expt. No.	Amt. taken (g)		Duration of reaction (days)	Duration of heating		Properties of reaction products		Yield (%)	Composition (%)	
	thiol	ether		hour	temp. (°C)	B.p. (°C)	Pressure (mm Hg)		(I)	(II)
9	6.2	20.0	20	—	Room	65-78	4	12.9	86.4	13.6
1	8.3	27.0	7	8	50	65-70	4	87	37.6	62.4
2	25.0	60.0	14	12	100	57-67	3	89.5	40.5	59.5

a small amount of unchanged ethanethiol were distilled off under reduced pressure. The residue distilled over completely at 57-67°/3 mm, weighed 58.4 g (89.5%), and contained, according to titration, 40.5% of 1-butoxy-1-(ethylthio)ethane. Fractional vacuum distillation of 55 g of this mixture through a column of 20 theoretical plates yielded:

Fraction I (in a cooled trap) 0.6 g; n_D^{20} 1.4439

Fraction II; b.p. 56.1-56.2° at 4 mm, 17.3 g; n_D^{20} 1.4476

Fraction III, b.p. 56.4-67.6° at 4 mm, 5.2 g; n_D^{20} 1.4473

Fraction IV, b.p. 67.6-68.2° at 3.9 mm, 4.5 g; n_D^{20} 1.4519

Fraction V, b.p. 67.8-68.2 at 3.5 mm, 25.1 g; n_D^{20} 1.4521

Fraction II was 1-butoxy-1-(ethylthio)ethane • n_D^{20} 1.4476; d_4^{20} 0.8897; found MR 48.79; calculated MR 48.76.

Found %: C 59.37; 59.29; H 11.04; 10.93; S 19.79; 19.70

$C_8H_{16}OS$. Calculated %: C 59.29; H 11.18; S 19.76

By titration with alkali after addition of excess of mercuric chloride, the content of monothioacetal was found to be 96.5%.

Fraction V was 1-butoxy-2-(ethylthio)ethane and did not give an acid reaction in presence of excess of mercuric chloride; n_D^{20} 1.4521; d_4^{20} 0.8981; found MR 48.76; calculated MR 48.76.

Found %: C 59.63; 59.71; H 11.16; 11.20; S 19.82; 20.09

$C_8H_{16}OS$. Calculated %: C 59.20; H 11.18; S 19.76

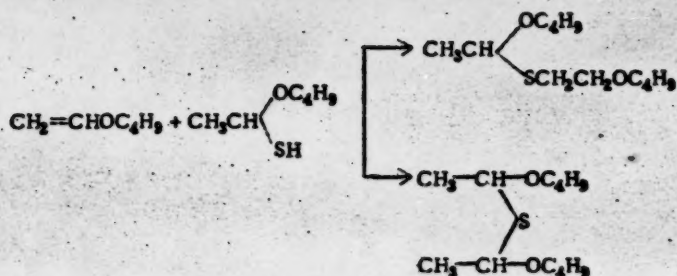
d) Butyl vinyl ether and 2-butoxyethylethanethiol



2-Butoxyethylethanethiol (0.8 g) [4a] was mixed in a small flask having a ground-in stopper with butyl vinyl ether (2 g). After 20 days, the excess of the ether was distilled off, and further distillation yielded a mixture of sulfides (1.2 g, 85.7%) having b.p. 118-124° at 3 mm; n_D^{20} 1.4552, i.e., the constants of a mixture of 1-butoxyethyl 2-butoxyethyl sulfide with bis(2-butoxyethyl) sulfide [4a]. Analysis by titration after addition of excess of mercuric chloride showed that the mixture contained 34.5% of 1-butoxyethyl 2-butoxyethyl sulfide.

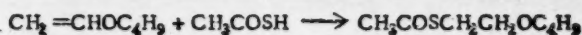
* In the literature the b.p. of this substance is given as 28-30°/2.5 mm [10]. It is probable that the authors were dealing with an impure product.

e) Butyl vinyl ether and 1-butoxyethylethanethiol



Butyl vinyl ether (4 g) was added to 1-butoxyethylethanethiol (2 g) having b.p. 52-53° at 20 mm; n_D^{20} 1.4428 [8], and after a week the products were treated as in the preceding experiment, yielding 2.1 g (60%) of a mixture of sulfides having b.p. 102-106° at 3 mm and n_D^{20} 1.4530, and giving a cream precipitate with mercuric chloride, which is a qualitative reaction for the simultaneous presence of α,β' -dialkoxy- and α,α' -dialkoxy-diethyl sulfides [4a, 4b]. Titration with alkali after addition of excess of mercuric chloride showed that the mixture contained 90.4% of 1-butoxyethyl 2-butoxyethyl sulfide and 9.6% of bis(2-butoxyethyl) sulfide. It was noted that in this experiment an appreciable amount (about 1 g) of resinous products were formed, thus reducing the yield of sulfides.

f) Butyl vinyl ether and thioacetic acid



Freshly distilled thioacetic acid (b.p. 87-90°; 9.3 g) was added to butyl vinyl ether (30 g) in a small flask having a ground-in stopper. The rise in temperature was so rapid that it was necessary to cool the mixture with ice water. After two days the reaction products were vacuum-fractionated. After removal by distillation of the excess of butyl vinyl ether, the following fractions were obtained:

Fraction I, b.p. 60-92° at 9.5 mm, 1 g

Fraction II, b.p. 92-98° at 9.5 mm, 19.5 g; n_D^{20} 1.4571

the yield of Fraction II being 90.7%.

Evidently, only 2-butoxyethyl thiolacetate was formed, for it was not found possible (by fractionation through a column of 20 theoretical plates) to isolate a fraction corresponding in properties to 1-butoxyethyl thiolacetate, previously synthesized by us from 1-butoxyethanethiol [8]. 1-Butoxyethyl thiolacetate has b.p. 61.7-62.3° at 3 mm; n_D^{20} 1.4560 and d_4^{20} 0.9664 [8]. Fractionation through the column of 23.1 g of the united products from two similar experiments gave:

Fraction I, b.p. 53.5-82.6° at 5.1 mm, 1.0 g; n_D^{20} 1.4420

Fraction II, b.p. 82.6-84.0° at 5.1 mm, 5.0 g; n_D^{20} 1.4600

Fraction III, b.p. 84.0-84.1° at 5.1 mm, 15.1 g; n_D^{20} 1.4605

Thus, the bulk of the substance distills over within a narrow range of temperature. Fraction III was found to have: d_4^{20} 0.9805; found MR 49.28; calculated MR 48.77.

Found %: C 54.43; 54.65; H 9.14; 9.15; S 17.95; 18.00

$\text{C}_8\text{H}_{16}\text{O}_2\text{S}$. Calculated %: C 54.51; H 9.15; S 18.19

Thioacetic acid unites vigorously with butyl vinyl ether with formation only of products formed by addition in the direction contrary to Markovnikov's rule.

SUMMARY

1. Methods have been developed for the synthesis from vinyl ethers and thiols of two series of sulfides: monothioacetals (1-alkoxy-1-(alkylthio)ethanes) and diethers of 2-mercaptoethanol (1-alkoxy-2-(alkylthio)ethanes).

2. It has been shown that the noncatalyzed addition of thiols to vinyl ethers in accord with Markovnikov's rule is a very slow reaction. The introduction of a catalyst, such as traces of sulfur dioxide, accelerates this reaction and leads to the quantitative synthesis of monothioacetals.

3. Addition of thiols in the direction contrary to that given by Markovnikov's rule is readily effected in a sealed evacuated ampoule. The reaction is greatly accelerated by rise of temperature, and is evidently catalyzed by traces of dissolved oxygen.

4. In presence of air, addition of thiols to vinyl ethers gives mixtures of "abnormal" and "normal" products, the former predominating. The composition of the mixture depends on the mixture of the vinyl ether and of the thiol taken.

5. The products of the oxidation by air of vinyl ethers and thiols do not accelerate abnormal addition, but, on the contrary, slow it down, which is in conflict with certain consequences of Kharash's peroxide theory.

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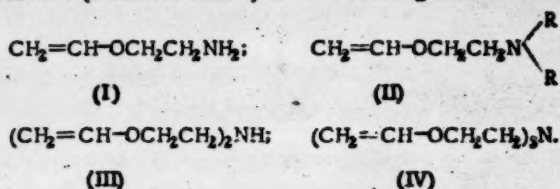
* See Consultants Bureau English translation, page 459 ff.

SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

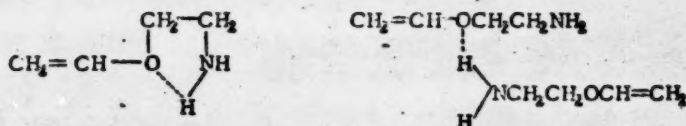
COMMUNICATION 3. NATURE OF THE DOUBLE BOND OF VINYL ETHERS OF ETHANOLAMINES

M. F. Shostakovsky and I. A. Chekulaeva

The present communication relates to an investigation into the synthesis and reactions of vinyl ethers of ethanolamines (2-aminoethanols) of the following structure:

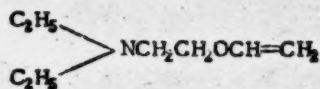


In the previous papers [1,2] it has been noted that the vinyl ether of 2-aminoethanol (monoethanolamine) (I) is less reactive than alkyl vinyl ethers. This is clearly seen from the course of such reactions as hydrolysis and interaction with alcohols. The peculiar behavior of the vinyl ether of 2-aminoethanol is to be explained by the presence in its molecule of a primary amino group in the β -position to the oxygen. The mutual influence of these groups may lead to the formation of intra- and inter-molecular hydrogen bonds according to the scheme:



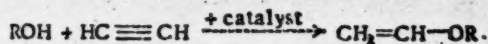
The presence of a hydrogen bond of this sort hinders the action of the catalyst at the oxygen atom of this vinyl ether and so weakens the activation effect of this compound required by the oxonium mechanism [3].

If this is the explanation of the phenomenon under examination, the double bond in N-substituted vinyl ethers (II), in which there are no mobile hydrogen atoms on the nitrogen, must approximate to a certain extent in character and behavior to the double bond of alkyl vinyl ethers. In order to verify this supposition, a study has been made of the properties of the vinyl ether of 2-(diethylamino)ethanol:



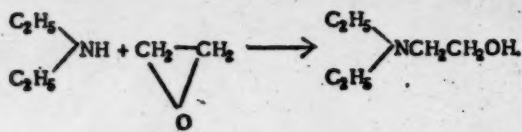
Only the boiling point of this substance is given in the literature [9]. No description has been given of its other properties and of the conditions for its synthesis.

We prepared the vinyl ether of 2-(diethylamino)ethanol by the vinylation of the corresponding alcohol by the reaction developed by Favorsky and Shostakovsky [4,2]

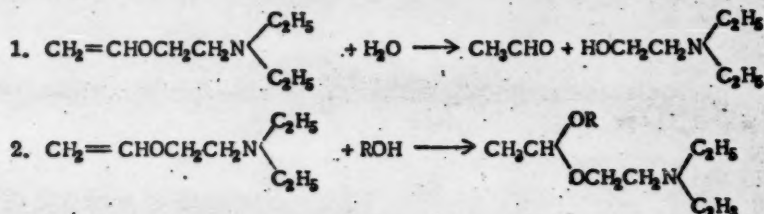


Reaction proceeds in presence of the potassium derivative of 2-(diethylamino)ethanol, giving an 85% yield of the vinyl ether. The use of a solvent (benzene) increases the yield of this vinyl ether to 95-98%. There is practically no catalytic vinylation of 2-(diethylamino)ethanol in presence of caustic potash, no doubt owing to the difficulty with which the potassium derivative of 2-(diethylamino)ethanol is formed under the conditions of vinylation.

The original 2-(diethylamino)ethanol was prepared from ethylene oxide and diethylamine [3,6,7]:



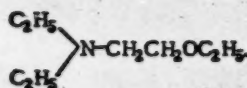
The chemical reactions of the vinyl ether of 2-(diethylamino)ethanol which were studied, its hydrolysis and addition reaction with alcohols, proceed according to the following equations:



It was found that the vinyl ether of 2-(diethylamino)ethanol, unlike that of 2-aminoethanol, is readily and completely hydrolyzed by 2% H_2SO_4 and is able to form acetals.

Thus, taking the hydrolysis and alcohol-addition reactions of the vinyl ether of 2-(diethylamino)ethanol as examples, we have shown that vinyl ethers of 2-aminoethanol in which there are no mobile hydrogen atoms on the nitrogen do indeed approximate in their properties to alkyl vinyl ethers. The presence, however, of two onium centers (O and N) has some effect also in this case. For example, the synthesis of acetals by reaction of the vinyl ether of 2-(diethylamino)ethanol with alcohols required more severe conditions than those required for alkyl vinyl ethers, and gave lower yields (13%) [8].

The structure of the vinyl ether of 2-(diethylamino)ethanol was proved not only by its hydrolysis and the synthesis of the acetal, but also by hydrogenation. This reaction was carried out at room temperature over Raney nickel as catalyst, and it led to the formation of the ethyl ether of 2-(diethylamino)ethanol:



EXPERIMENTAL

Synthesis of 2-(diethylamino)ethanol

Ethylene oxide (60-70 g) was passed over a period of 4-5 hours into a stirred solution of diethylamine (75 g, b.p. 55-56°; n_D^{20} 1.3870) in water (250 ml). The mixture became warm, and the reaction temperature was maintained at 5-10° by ice-water cooling. The product obtained was salted out with caustic potash, separated from the water, and neutralized by a stream of carbon dioxide. The precipitate that formed was filtered off, and

the filtrate was distilled, yielding 2-(diethylamino)ethanol $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{N-CH}_2\text{CH}_2\text{OH} \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$ (60 g, 50%) as a colorless liquid having a sharp odor. Its constants were: b.p. 159-161°; n_D^{20} 1.4412; d_4^{20} 0.8838; found MR 35.03; calculated $\text{C}_6\text{H}_{15}\text{ON}$ MR 35.37. Data in the literature: b.p. 160° at 741 mm; d^{25} 0.8800; n_D^{25} 1.4389 [6]; b.p. 163° at 760 mm; d_{25}^{25} 0.8601; n_D^{25} 1.4400 [7].

Vinylation of 2-(diethylamino)ethanol

Vinylation was carried out in a stainless-steel rotating autoclave. 2-(Diethylamino)ethanol (b.p. 159-161°; n_D^{20} 1.4412), catalyst (10% on the amount of the original 2-aminoethanol), and a two-fold amount of solvent (benzene) were introduced into the autoclave, and acetylene was passed in up to a pressure of 15 atm; the autoclave was then heated. Caustic potash or the potassium derivative of 2-(diethylamino)ethanol was used as catalyst. The potassium

derivative was prepared in a round-bottomed flask with stirrer by addition of potassium to 2-(diethylamino)ethanol, taken in excess, and it was introduced into the autoclave as a solution. The temperature of the vinylation reaction was maintained at 140-150°. Vinylation was continued until the calculated amount of acetylene had been absorbed. Excess of acetylene brought about resinification. The results of the vinylation are given in the table.

TABLE

Expt. No.	Catalyst	Solvent	% Yield of crude vinyl ether	Amt. of resin (% on original 2-aminoethanol)
1	Potassium deriv.	Benzene	95-98	3-5
2	Potassium deriv.	No solvent	83-85	12-15
3	Caustic potash	Benzene	0-0	15-20

The reaction product was a yellowish-red mobile liquid. It was fractionated, at first under reduced pressure, and then at atmospheric pressure. The fraction of b.p. 154-159° at 760 mm was collected, and, with a view to its purification from traces of the original alcohol, it was treated with sodium in the cold and again distilled. The yield of pure product when the vinylation was carried out in benzene in presence of the potassium derivative of the 2-aminoethanol was 93-95%. The analytical results corresponded

to the vinyl ether of 2-(diethylamino)ethanol $\text{C}_2\text{H}_5 \text{---} \text{N} \text{---} \text{CH}_2\text{CH}_2\text{OHC}=\text{CH}_2$; b.p. 155-157°; n_D^{20} 1.4328; d_4^{20} 0.8396; found MR 44.31; calculated $\text{C}_8\text{H}_{17}\text{ON}$ MR 44.26. Data in the literature: b.p. 51-55° at 15 mm [9].

Found %: C 67.27; 67.21; H 12.02; 12.24; N 9.90; 10.14
 $\text{C}_8\text{H}_{17}\text{ON}$, Calculated %: C 67.10; H 11.96; N 9.78

The vinyl ether of 2-(diethylamino)ethanol is a colorless mobile liquid having a feeble odor; it is soluble in benzene and ether. It was hydrolyzed by 2% H_2SO_4 at room temperature, and the acetaldehyde formed was accounted for quantitatively by the bisulfite method [10]

Ester found (%): 100.2, 98.5

Hydrogenation of the Vinyl Ether of 2-(diethylamino)ethanol

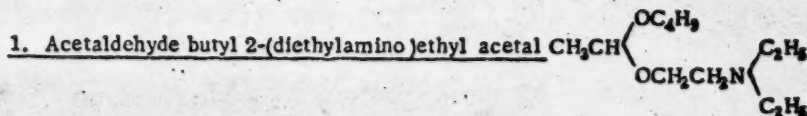
The vinyl ether (b.p. 155-157°; n_D^{20} 1.4328) (13 g) and Raney nickel (0.6 g) were introduced into a 150 ml rotating autoclave, and hydrogen was passed in up to a pressure of 50 atm. Hydrogenation proceeded at room temperature, the theoretical amount of hydrogen being absorbed in 12 hours. The reaction product was filtered off from the catalyst and was distilled at atmospheric pressure. The fraction boiling at 151-155° was collected, and this, after treatment with sodium in the cold, yielded 9.1 g (70%) of a product having the following properties: b.p. 154.5°; n_D^{20} 1.4176; d_4^{20} 0.8145; found MR 44.88; calculated $\text{C}_8\text{H}_{19}\text{ON}$ MR 44.73.

Found %: C 66.27; 65.90; H 13.42; 13.07; N 9.26; 9.50
 $\text{C}_8\text{H}_{19}\text{ON}$, Calculated %: C 66.17; H 13.19; N 9.64

The analytical results for this product corresponded to the ethyl ether of 2-(diethylamino)ethanol:

$\text{C}_2\text{H}_5 \text{---} \text{N} \text{---} \text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5$. Data in the literature: b.p. 63-64° at 25 mm; n_D^{20} 1.4179 [11].

Synthesis of Acetals from the Vinyl Ether of 2-(Diethylamino)ethanol



a) Synthesis of the acetal by the reaction of the vinyl ether of 2-(diethylamino)ethanol with butanol in presence of concentrated hydrochloric acid. The vinyl ether of 2-(diethylamino)ethanol (b.p. 155-157°; n_D^{20} 1.4328) (13 g, i.e. 0.09 mole) and butanol (b.p. 116-117°; n_D^{20} 1.3990) (6.7 g, i.e. 0.09 mole) were introduced into a round-bottomed flask fitted with stirrer and thermometer. Concentrated hydrochloric acid (3-4 drops) was added under

stirring, and the temperature was found to rise from 24° to 26°. The reaction mixture was then heated at 50° for three hours; it darkened considerably. On the next day the reaction product was neutralized with magnesium carbonate, the precipitate was filtered off, and the filtrate (19.1 g) was distilled, at first at atmospheric pressure, and then under reduced pressure. The following fractions were collected:

Fraction I, b.p. 100-125°;	n_D^{20} 1.4087;	3.0 g
Fraction II, b.p. 125-145°;	n_D^{20} 1.4160;	4.8 g
Fraction III, b.p. 145-160°;	n_D^{20} 1.4322;	7.1 g
Fraction IV, b.p. 60-90°/3.5 mm;	n_D^{20} 1.4129;	0.2 g
Fraction V, b.p. 90-100°/3.5 mm;	n_D^{20} 1.4292;	2.7 g
Fraction VI, b.p. 100-110°/3.5 mm;	n_D^{20} 1.4363;	0.4 g
Fraction VII, resin		0.9 g
		<hr/> 19.1 g

Fraction V, after treatment with sodium in the cold, yielded 2.6 g (13.7%) of the required acetal as a colorless liquid having the following constants: b.p. 90-92° at 4.5 mm; n_D^{20} 1.4275; d_4^{20} 0.8670; found MR 64.42; calculated $C_{12}H_{21}O_2N$ MR 64.84.

	Found %:	C 66.46; 66.39; H 12.50; 12.42; N 6.45; 6.31
$C_{12}H_{21}O_2N$	Calculated %:	C 66.31; H 12.53; N 6.44

The acetal was hydrolyzed with 2% H_2SO_4 at room temperature, and the acetaldehyde formed was determined quantitatively by the bisulfite method:

Acetal found (%): 100.6, 97.2

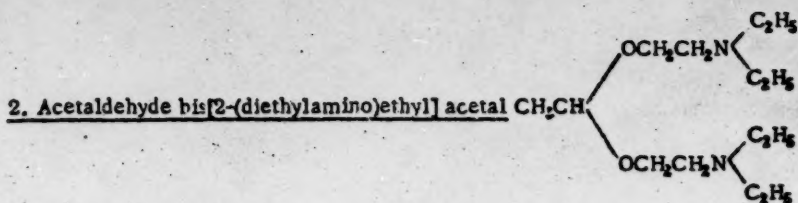
Fractions I, II, and III were mixtures of butanol and the vinyl ether of 2-(diethylamino)ethanol; removal from them of alcohol by means of sodium followed by distillation yielded 9 g of the vinyl ether of 2-(diethylamino)ethanol, b.p. 155-157°; n_D^{20} 1.4328.

b) Synthesis of the acetal from the vinyl ether of 2-(diethylamino)ethanol and butanol by heating in absence of catalyst. The vinyl ether of 2-(diethylamino)ethanol (b.p. 155-157°; n_D^{20} 1.4328) (2.3 g, i.e. 0.016 mole) was heated with butanol (b.p. 116-117°; n_D^{20} 1.3990) (1.2 g, i.e. 0.016 mole) in an ampoule at 230-250° for 15 hours; yellowing occurred. The contents of the ampoule were distilled, at first under reduced pressure, and then at atmospheric pressure. The following fractions were collected:

Fraction I, b.p. 115-117°;	n_D^{20} 1.3995;	0.4 g
Fraction II, b.p. 117-150°;	n_D^{20} 1.4180;	1.2 g
Fraction III, b.p. 150-156°;	n_D^{20} 1.4324;	1.0 g
Fraction IV, b.p. 60-85°/3 mm;	n_D^{20} 1.4130;	0.1 g
Fraction V, b.p. 85-90°/3 mm;	n_D^{20} 1.4280;	0.5 g
Fraction VI, resin		0.3 g
		<hr/> 3.5 g

Redistillation of Fraction V yielded 0.45 g (13%) of the acetal required; it had b.p. 90-92° at 4.5 mm; n_D^{20} 1.4275 (see previous synthesis). Fraction I was butanol. Fractions II and III were treated with sodium and distilled, yielding 1.8 g of the vinyl ether of 2-(diethylamino)ethanol, b.p. 155-157°; n_D^{20} 1.4328.

2. Acetaldehyde bis[2-(diethylamino)ethyl] acetal



The acetal was prepared by heating 15.1 g (0.105 mole) of the vinyl ether of 2-(diethylamino)ethanol (b.p. 155-156°; n_D^{20} 1.4328) with 12.2 g (0.105 mole) of 2-(diethylamino)ethanol (b.p. 159-161°; n_D^{20} 1.4412) in presence of concentrated hydrochloric acid. The reaction temperature was maintained at 100-105° for four hours. The reaction products were treated as in the previous experiment. Fractionation of 24 g of the reaction mixture yielded:

Fraction I, b.p. 155-160°:	n_D^{18} 1.4382; 22.4 g
Fraction II, b.p. 115-116° at 4.5 mm; n_D^{19} 1.4440;	1.5 g (6.2%)
Fraction III, resin	0.1 g
	<hr/> 24.0 g

Fraction II was a light-yellow liquid, which, according to the analytical results, corresponded to the required acetal: b.p. 115-116° at 4.5 mm; n_D^{20} 1.4440; d_4^{20} 0.8886; found MR 77.83; calculated $\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_2$ MR 78.01.

Found %:	C 64.89;	H 12.80;	N 11.22
$\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_2$. Calculated %:	C 64.57;	H 12.40	N 10.76

Fraction I was a mixture of the original 2-(diethylamino)ethanol and its vinyl ether.

SUMMARY

1. Conditions of vinylation of 2-(diethylamino)ethanol have been found that permit the preparation of its vinyl ether in 93-95% yield.
2. The vinyl and ethyl ethers of 2-(diethylamino)ethanol have been prepared and characterized.
3. It has been shown that the vinyl ether of 2-(diethylamino)ethanol has a greater tendency to hydrolyze and form acetals than the vinyl ether of 2-aminoethanol.
4. The butyl-2-(diethylamino)ethyl acetal and the bis[2-(diethylamino)ethyl] acetal of acetaldehyde have been synthesized.

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CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE BY OXIDIZING AGENTS

COMMUNICATION 8. CHEMICAL CHANGES IN CELLULOSE PRODUCED BY OXIDATION WITH HYDROGEN PEROXIDE

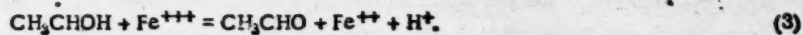
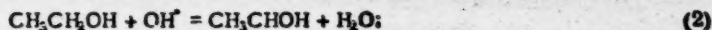
V. I. Ivanov, E. D. Kaverzneva, and Z. I. Kuznetsova

Hydrogen peroxide is one of the oxidizing agents that have received practical application in the bleaching of cellulosic materials and fibers. Hydrogen peroxide gives the best results when we require a good white in association with high fiber qualities. In our work we have found that a combined hypochlorite-peroxide bleach applied to wood sulfite celluloses that are difficult to bleach yields a high-quality product. It is therefore of both scientific and practical interest to elucidate the chemical processes occurring during the action of peroxide on cellulose.

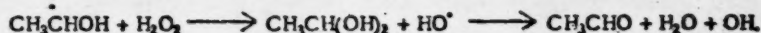
Hydrogen peroxide is not a specific oxidant, and, under sufficiently severe conditions, oxidation may lead to splitting of carbon-carbon bonds, with complete breakdown of the whole molecule. Ferrous salts catalyze the oxidation reaction. The mechanism of the action of hydrogen peroxide has not yet been fully elucidated. According to the most generally accepted theory, the oxidation of organic substances by hydrogen peroxide in an acid medium is initiated by the reaction between Fe^{++} and H_2O_2 , which yields a free hydroxyl radical [1]:



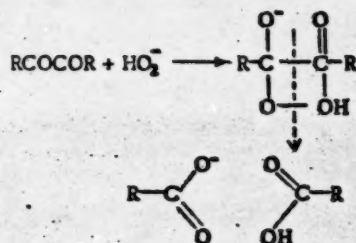
The reaction then develops by a chain mechanism:



According to another variant, oxidation of the organic radical may proceed by reaction with H_2O_2 or OH^\cdot



Hydrogen peroxide has its least oxidizing power in neutral solution. Monohydric primary alcohols, for example, do not react under these conditions. In alkaline solution hydrogen peroxide oxidizes compounds of a type that is scarcely affected in acid medium, for example -phenylglyoxylic acid $\text{C}_6\text{H}_5\text{COCO}_2\text{H}$. The mechanism of the reaction in an alkaline medium has not, as yet, received much investigation. The radical mechanism for this case has been disputed, and the theory that the anion HO_2^- is the active oxidizing agent has been advanced [2]. For the oxidation of a diketone, the following reaction scheme has been proposed:



On the basis of numerous experimental researches on the oxidation of organic compounds with hydrogen peroxide, the following conclusions may be drawn concerning the character of the action of this oxidizing agent on various functional groups. In acid medium in presence of Fe^{++} , hydrogen peroxide oxidizes a primary OH group in monohydric alcohols to an aldehyde or, by further reaction, to a carboxyl group [3]. In 0.2 N H_2SO_4 at 0°, the concentrations of ethanol and H_2O_2 being molar, 41% of the peroxide present was expended in oxidation to acetaldehyde, and the same amount went in the oxidation to acetic acid [4].

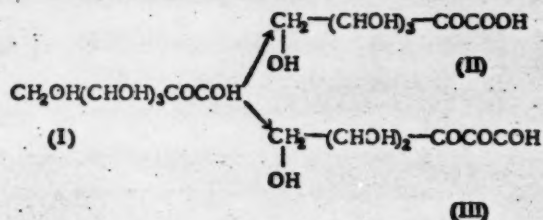
In the oxidation of polyhydric alcohols, reaction occurs first at a primary OH group: glycerol yields glyceraldehyde [5]. The appearance of an aldehyde group, however, reduces the stability of the adjacent secondary OH group, which is then oxidized in its turn. Thus, of the three different functional groups of glyceraldehyde, the least stable to oxidation under these conditions is the secondary alcohol group. The hydroxypyruvaldehyde formed is oxidized then to the acid, and is decarboxylated and decomposed into smaller molecules.

An isolated keto group or an isolated double carbon-carbon linkage is not generally broken down by hydrogen peroxide. When the keto group is conjugated with a C=C or C=O bond, alkaline oxidation rapidly leads to breakdown of the carbon chain [6]. Hence, α -diketones, α -keto aldehydes, and α -keto carboxylic acids are rapidly decomposed in presence of peroxide.

According to Waters [1], in the oxidation of α -glycols, in addition to the main reaction of diketone formation, there is another reaction: splitting of the carbon chain by free OH radicals with formation of aldehydes. Thus, 2,3-butanediol yields 2,3-butanedione and a small amount of acetaldehyde.

In the oxidation of polyfunctional carbohydrate systems and polyhydroxy acids, the course of the reaction is complicated. The first stage of the oxidation of hexoses in acid medium appears to be glucosone; 2-keto acids are generally obtained from hydroxy acids. Here therefore, as in the case of glyceraldehyde, adjacency to a carbonyl or carboxyl group activates a secondary hydroxyl.

It is difficult to establish the further stages of the oxidation of glucosone (I). Kuchlin [7] assumes that oxidation both of the aldehyde and of the secondary hydroxyl group may occur, according to the concentration of the peroxide:



He isolated 2-ketogluconic acid (II), but he advances the compound III as an intermediate product on the basis of the decomposition products found. Thus, predominance of the oxidation of the secondary hydroxyl group or of the aldehyde group depends on the concentration conditions of the reaction.

A certain difference in the direction of the oxidation reaction in presence and in absence of iron may be seen from these experiments of Kuchlin [7] and from work by Jolles [8] on the oxidation of glucose. For oxidation with H_2O_2 in a weakly acid medium in absence of iron, Jolles obtained glucuronic acid: the primary OH group was oxidized to COOH, but the aldehyde group remained unchanged. Kuchlin, working with H_2O_2 in presence of iron, obtained glucosone in the first stage of the reaction, i.e. a secondary OH group was oxidized. However, neither of these authors gives any indication of the amounts of the isolated compounds and of the presence of other oxidation products.

The elementary chain of cellulose contains primary and secondary alcohol groups, glucoside (acetal) bonds, and terminal aldehyde groups. As the oxidation of cellulose by peroxide proceeds in a heterogeneous medium, the factors determining the course of the reaction comprise not only the chemical structure of the molecule, but also the spatial configuration of the macromolecules as a whole and their relative dispositions, which determine the accessibility of particular sections of the chain to the penetration of the oxidizing agent. Mere analogy to the simplest carbohydrates is therefore insufficient for the elucidation of the oxidative breakdown of cellulose under the action of peroxide.

There is a paucity of data in the literature on this question. It is generally considered that hydrogen peroxide reacts with cellulose only in strongly alkaline solution (8% NaOH) [9]. There is then a fall in the viscosity in cuprammonium solution of the treated cellulose. Estimations have been made of the carboxyl

TABLE 1

General Table of the Analyses of Oxycellulose Produced by Hydrogen Peroxide Oxidation*
All results in equivalents per 100 glucose residues

Expt. No.	Oxidation conditions	Reaction of medium	Yield (%)	Coeff. of polymerization	Ash (%)	COOH content			Content of			Notes
						total	uronic	non-uronic	carbonate group	aldehyde group	keto group	
1	5 hrs, 40°	pH 4.6	—	244	0.04	0.72	0.53	0.19	1.43	0.61	0.76	Cotton
2	5 hrs, 40°	Slightly acid	97.8	220	0.11	1.15	1.01	0.14	2.03	1.39	0.64	Sulfite cellulose
3	5 hrs, 40°	"	—	—	—	0.97	0.89	0.08	1.99	—	—	"
4	5 hrs, 40°	pH 7	100	1800	0.09	0.13	0.22	—	0.66	—	—	Cotton
5	19 hrs, 40° + 119 hrs 25°	Ditto	97.7	680	0.08	0.19	0.46	—	1.19	0.43	0.76	"
6	15 hrs, 40° + 81 hrs, 18°	"	99.7	390	0.08	0.29	0.85	—	0.98	0.18	0.80	Cellulose oxidized with 18% H ₂ O ₂
7	22 hrs, 40° + 98 hrs, 18°	"	98.5	265	0.07	0.47	0.72	—	1.29	0.64	0.65	Ditto, 14% H ₂ O ₂
9	48 hrs, 18° 2% NaOH	Alkaline	95.6	265	0.09	0.76	0.37	0.39	0.87	0.57	0.30	Cotton
10	5 hrs, 40° 8% NaOH	"	85.5	175	0.08	0.81	0.58	0.23	1.05	0.52	0.53	"
11	5 hrs, 40° 2% NaOH	"	93.9	244	0.12	0.89	0.29	0.60	1.10	0.32	0.78	"
12	5 hrs, 40° 2% NaOH	"	95.7	—	0.08	0.86	0.22	0.64	0.68	0.53	0.15	"
13	111 hrs, 40° + 425 hrs, 18°; 0.2% NaOH	"	95	162	0.06	1.12	0.64	0.48	0.95	0.61	0.34	"
	Unoxidized cotton			3500	0.19	0.14	0.30		0.50	0.30	0.20	
	Unoxidized sulfite cellulose			800	0.20	0.32	0.76		—	—	—	

* The H₂O₂ concentration was 5%, except in Experiments 6 and 7; the liquor ratio was 40:1; FeSO₄ was added; in Experiments 1-3 an acetate buffer was added, and in Experiments 4-8 a borate buffer of pH 6.8 was added.

groups in oxycelluloses obtained by peroxide oxidation in alkaline medium [10]: after a 5 hr oxidation at 80° with 0.7% H₂O₂, the oxycelluloses contained 0.06-0.08% of COOH groups.

In a recently published investigation of the oxidation of cellulose by hydrogen peroxide in alkaline medium, erythronic acid and other still further degraded products were isolated from the decomposition products [11]. There are also a number of patents and articles in which methods of bleaching celluloses and wood pulps with peroxides are described [12]; questions concerning the chemical changes occurring during the oxidation are not really considered in these publications.

TABLE 2

Distribution of Aldehyde Groups in Oxycelluloses Prepared by H_2O_2 Oxidation

Expt. No.	Conditions of oxidation in 5% H_2O_2	Coefficient of polymerization	Content per 100 glucose residues of			No. in one chain of		
			CHO	Uronic COOH		CHO (total)	CHO at C_2	other CHO
				before NaIO oxidn.	after oxidation			
15	71 hrs, 62°, pH 4.6	250	0.83	0.47	0.64	2.1	0.43	1.67
1	5 hrs, 40°, pH 4.6	244	0.67	0.58	0.63	1.5	0.03	1.47
5	19 hrs, 40° } pH 7	680	0.43	0.46	0.47	2.9	0.07	2.87
	119 hrs, 25° }							
8	52 hrs, 40° } pH 7	340	0.58	0.47	0.50	1.97	0.10	1.87
	230 hrs, 18° }							
9	48 hrs, 18° 2% NaOH	265	0.57	0.37	0.32	1.5	0	1.50
10	5 hrs, 40° 8% NaOH	175	0.52	0.58	0.57	0.9	0	0.9
11	5 hrs, 40° 2% NaOH	244	0.32	0.29	0.41	0.8	0.29	0.51
14	11 hrs, 40° } 10% NaOH	162	0.45	0.36	0.58	0.7	0.36	0.34
	60 hrs, 18° }							

EXPERIMENTAL

We have studied quantitative changes in the functional groups present in cotton cellulose in conjunction with the changes occurring in the viscosity of its cuprammonium solution, the cellulose being oxidized with hydrogen peroxide under various conditions. The method of investigation was the same as that used in our previous work on the oxidation of cellulose with sodium hypochlorite. The material used in the experiments was cotton cellulose freed from impurities by means of the usual alkaline treatment and by extraction with dichloroethane. After the oxidation (for conditions see Table 1), the oxycelluloses were demineralized in 0.5% acetic acid, washed free from acid, dried at room temperature, and analyzed for their contents of the following functional groups:

- 1) Total carboxyl groups by the calcium acetate method [13].
- 2) Uronic carboxyl groups by a micro variant of the method of decarboxylation with 12% HCl [14].
- 3) Aldehyde groups (iodometrically; borate buffer, pH 9.5; two hours at 25°; titration with 0.01 N $Na_2S_2O_3$ [15].
- 4) Total carbonyl groups by condensation with hydroxylamine hydrochloride and titration of the free HCl (three hours at 20-25°, pH 5-6; titration with 0.1 N HCl to pH 3.5 (Bromo Phenol Blue)) [16].
- 5) Nitrogen, after condensation with hydroxylamine, by Kjeldahl. The amount of nitrogen found varied on the average from about 60% to 80% of the amount calculated from the content of carbonyl groups determined by the titration method. The reason for this discrepancy is not altogether clear and we are studying it.
- 6) Ketone groups from the difference in the carbonyl content (according to nitrogen) and the aldehyde content.
- 7) The coefficient of polymerization, determined from the cuprammonium viscosity by the formula
$$p = \frac{\eta}{d \cdot c \cdot K_m}$$
, where η is the specific viscosity $\frac{\eta_1 - \eta_0}{\eta_0}$, K is taken to be $5 \cdot 10^{-4}$, and c is the concentration of cellulose (g/l).

In most of the experiments the oxidation of the cellulose was carried out in presence of catalyst (0.01-0.1% $FeSO_4$ on the cellulose). Under practical bleaching conditions traces of iron are always present, i.e., the reaction must proceed by the catalytic-oxidation mechanism. We give a general table of the main analytical results (Table 1).

TABLE 3

Content of Ketone Groups in the Oxidation of Cellulose
(in equivalents per 100 glucose residues)

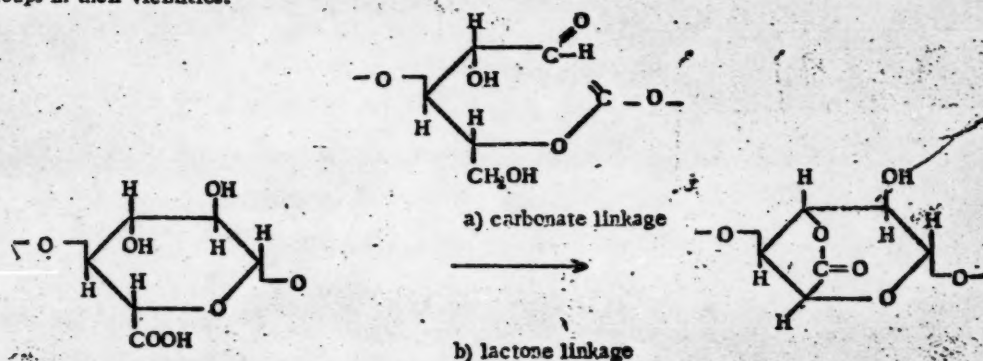
Expt. No.	Conditions of oxidation	Content of			CO/COOH
		COOH total	CHO	ketone groups	
16	Original cotton	0.14	0.40	0.15	1
	Oxidation in acid medium	0.22	0.83	0.35	1.6
1	Ditto	0.72	0.67	0.76	1.0
2	"	1.15	1.13	0.90	0.8
5	Oxidation in neutral medium	0.19	0.43	0.76	4.0
6		0.29	0.18	0.80	2.8
7		0.47	0.64	0.65	1.4
8	Oxidation in alkaline medium	0.52	0.58	0.82	1.6
9		0.76	0.57	0.30	0.34
10	Ditto	0.81	0.52	0.53	0.65
12	"	0.86	0.53	0.15	0.17
13	"	1.13	0.61	0.34	0.35
14	"	1.19	0.45	0.10	0.08

It may be noted as a general characteristic of peroxide-oxidized celluloses that even under very severe oxidation conditions (5% H_2O_2 in 10% NaOH at 40° for more than 10 hours, or at 90° for 2 hours) the number of oxidized groups remains very low. The maximum carboxyl content in our experiments was 0.34%, or 1.19 equivalents per 100 glucose residues. Oxycelluloses can be obtained by oxidation with an alkaline solution of hypochlorite which have a 1% COOH content, i.e. more than 4 equivalents per 100 glucose residues.

When the total content of COOH groups was determined by the calcium acetate method and the uronic carboxyls were separately estimated by decarboxylation with 12% HCl, the same phenomenon was found as was found also by us for hypochlorite oxidation: for oxidation in a neutral medium, the content of uronic carboxyl groups was higher than the total COOH content of the preparation. There was a difference from the behavior found for hypochlorite oxidation in that whereas the discrepancy extended to acid and neutral oxidation in the case of hypochlorite, it occurred

in the present case only for solutions in the neutral region. In an acid medium, there was already a certain preponderance of total COOH content over uronic COOH content.

The causes of this phenomenon were studied by us for oxycelluloses prepared by hypochlorite oxidation [17], and it may be supposed that the same causes account for the increased uronic COOH contents in peroxide oxidation. These causes are: a) the presence of carbonate groups in the constitution of the oxycelluloses oxidized in acid and neutral media, and b) the presence of lactone (ester?) linkages between the uronic carboxyls and hydroxyl groups in their vicinities:



Both of these linkages constitute blocked acid groups and do not interact with calcium acetate. During heating with 12% HCl both of them give rise to CO_2 , giving an exalted value for the free uronic COOH.

As will be seen from the analyses given in Table 1, all the oxycellulose preparations contained aldehyde groups. It follows from the fact that the uronic carboxyl content showed a tendency to rise when supplementary oxidation of aldehyde groups with hypodite was effected (Table 2) that a part of the aldehyde groups are to be found at the 6-positions of the glucose residues. Most of the aldehyde groups are converted by oxidation into

TABLE 4

Effect of pH on the Rate of Oxidation of Cellulose by H_2O_2

pH during oxidation	Atoms of oxygen bound per 100 glucose residues	Degree of polymerization	Yield of oxycellulose %	Content (per 100 glucose residues)	
				COOH group	CHO + CO group
4.6	3.23	244	—	0.72	1.43
7.0	1.09	1800	100	0.13	0.66
12	3.15	244	93.9	0.89	1.10

Experimental conditions: 5% H_2O_2 ; liquor ratio 40:1; $FeSO_4$ and buffer added; 5 hrs at 42°.

TABLE 5

Effect of Prolonged Oxidation on the Content of Functional Groups in Oxycellulose (in equivalents per 100 glucose residues)

Conditions of oxidation	Content of				Degree of polymerization
	COOH total	COOH uronic	aldehyde group	ketone group	
Neutral medium, 40°					
5 hrs.	0.13	0.22	—	—	1800
19 hrs.	0.19	0.46	0.43	0.76	680
51 hrs.	0.52	0.47	0.58	0.82	340
Strongly alkaline medium, 40°					
5 hrs.	0.81	0.58	0.53	0.53	175
11 hrs.	1.19	0.35	0.45	0.10	162

TABLE 6

Content of Individual Functional Groups in Oxycelluloses and in the Alkali-soluble Fractions that Go into Solution during the Oxidation (in equivalents per 100 glucose residues)

Content of	Insoluble fraction	Soluble fraction	Notes
COOH, total	0.19	4.14	Oxidation 5 hrs, 40° in 8% NaOH
COOH, uronic	0.58	1.8	Oxidation 11 hrs, 40° in 10% NaOH
Aldehyde group	0.48	27.9	Oxidation 2 hrs, 90° in 0.5% NaOH

in acid and neutral media, and undergoes little change in alkaline media.

It will be seen from Table 3 that in cellulose oxidized in neutral medium ketone groups predominate over carboxyls; there are relatively fewer of them in acid medium, and in alkaline medium they disappear particularly rapidly. At the same time, the number of nonuronic carboxyls increases most rapidly for oxidation in alkaline medium. The positive qualitative reaction for the endiol grouping with a phosphoarsenotungstic reagent gives reason to suppose that a part of the ketone groups present belong to hydroxy ketone groupings that are able to isomerize into endiol groupings in a strongly alkaline medium.

* In addition to the carbonyl groups, the lactone groups present in the oxycelluloses may react with hydroxylamine. The figures for ketone groups may therefore be somewhat too high.

nonuronic carboxyls. It is possible on the basis of the coefficient of polymerization, with the usual proviso concerning the approximate nature of this method, to calculate the number of aldehyde groups in the average chain of the oxycellulose macromolecule. When the 6-aldehydes are taken into consideration, there remain more aldehyde groups than can on the average be found placed at the ends of chains (except in alkaline oxidation), and it must therefore be supposed that there are also present aldehyde groups formed by oxidation with rupture of the pyran ring, and this we have confirmed by experiments on methyl glucoside.

The figures given in Table 2 have, however, no absolute significance, since oxidation with sodium hypiodite leads to a loss of carboxyl groups owing to a certain amount of dissolution of the low-molecular-weight fractions of the preparations.

When hydrogen peroxide acts upon cellulose, ketone groups are formed. They arise at the very beginning of the oxidation: the content of these then rises slightly.

The rate of the oxidation of cellulose by hydrogen peroxide depends on the pH of the medium. This is shown in Tables 4 and 5. Oxidation proceeds vigorously in strongly alkaline and weakly acid media, and only very slowly in neutral media.

As oxidation is intensified, the most oxidized units of the chains break down and go into solution. This will be seen by comparing the content of functional groups in the water-insoluble oxycellulose with that in its soluble fraction, which separates when its solution is carefully acidified.

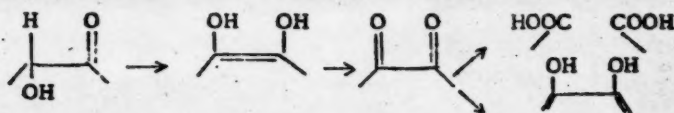
The high content of functional groups of all types in the soluble fractions of the oxycelluloses, as compared with the insoluble part is characteristic. For this reason the chemical composition of celluloses obtained after oxidation is often a poor guide to the extent of the oxidative reactions that have occurred.

Addition of catalyst greatly increases the oxidation process. It will be seen from Table 7 that in the last experiment, in which FeSO_4 was added, oxidation went appreciably further than in the first two experiments, in spite of the shorter duration of the experiment and the lower temperature.

In alkaline medium, the catalyst particularly accelerates the oxidation of secondary OH groups with rupture of the pyran ring and formation of nonuronic carboxyls. This conclusion is in full accord with the results of our investigations on the oxidation of methyl glucoside.

Thus, when cellulose is oxidized with H_2O_2 , the same functional groups are oxidized as in the case of the simplest sugars. In the first place, the 6-primary alcohol groups are oxidized to aldehyde groups, and the 2- and 3-secondary OH groups are oxidized to ketone groups. Theoretical considerations indicate that the 2- and 3-hydroxyls are not equivalent, and the 2-hydroxyl should oxidize more readily. This conclusion is in accord with the experimental results obtained for the oxidation of glucose [3]. The formation of ketone groups indicates that in the first stages oxidation of the secondary hydroxyls proceeds without rupture of the pyran ring.

On the basis of considerations given previously [17], it is most probable that the further oxidative breakdown of the pyran ring in strongly alkaline medium ($\text{pH} > 11$) passes through the stages of endiol and diketone:



However, as pointed out above, there are certain indications that when cellulose and also methyl glucoside is oxidized with hydrogen peroxide aldehyde groups are formed at the 2- and 3-positions of the glucose residues. It is therefore probable that breakdown of the pyran ring through the ketone stage is accompanied by a certain amount of oxidative rupture of the ring with formation of two aldehyde groups, as in the reaction established for glycols:

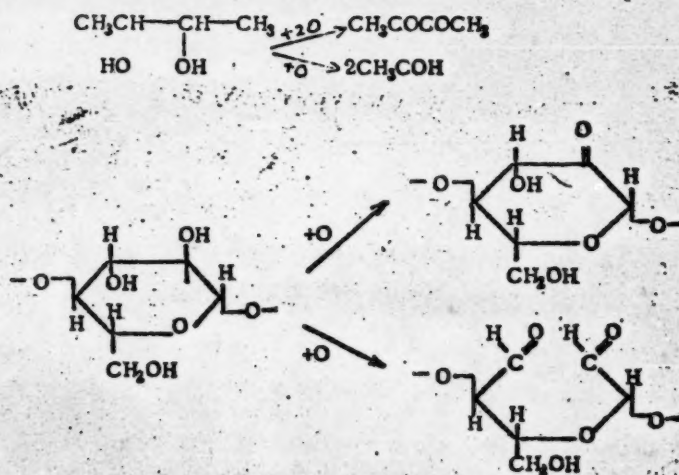


TABLE 7

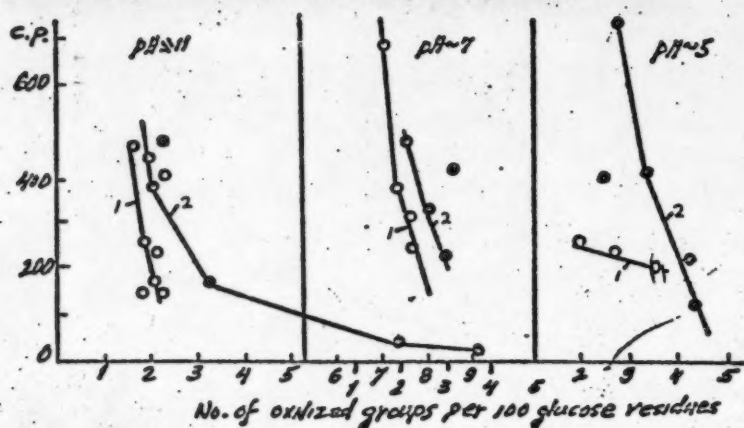
Effect of Catalyst (FeSO_4) on the Oxidation of Cellulose with H_2O_2 in Alkaline Medium ($\text{pH} > 11$)

Experimental conditions	COOH group content per 100 glucose res.			Coefficient of polymerization	Yield (%)
	total	uronic	nonuronic		
2.5% H_2O_2 , 60°, 10 hrs, without FeSO_4	0.18	0.29		408	—
5% H_2O_2 , 60°, 30 hrs, without FeSO_4	0.29	0.25	0.04	236	97
5% H_2O_2 , 40°, 5 hrs with addition of FeSO_4	0.89	0.29	0.60	244	93.8

TABLE 8

The Ratio CHO/COOH in Oxycelluloses Formed by Oxidation with NaClO and H_2O_2

Prep. No.	Oxidation conditions	CHO/COOH	Prep. No.	Oxidation conditions	CHO/COOH
	Oxidation with H_2O_2			Oxidation with NaClO	
1	In acid medium	0.93	4	In acid medium	1.23
2	" " "	1.20	1	" " "	1.40
9	In alkaline medium	0.75	7	" " "	1.39
10	" " "	0.64	1a	" " "	1.20
11	" " "	0.36	6	In alkaline medium	0.42
12	" " "	0.60	3	" " "	0.24
13	" " "	0.54	9	" " "	0.12
14	" " "	0.38	"b"	" " "	0.16
16	" " "	0.70	3a	" " "	0.15



Relation between coefficient of polymerization (c.p.) and extent of oxidation:

1) Oxidation with H_2O_2 ; 2) oxidation with NaClO .

cellulose when oxidized with hypochlorite. The chemical properties of the oxycelluloses obtained depend in the first place on the pH during oxidation; the nature of the oxidizing agent — H_2O_2 or NaOCl — affects essentially only the quantitative characterization of the properties of the oxycelluloses formed. But in certain respects a qualitative difference is to be observed also. For example, in oxycelluloses obtained by oxidation in an acid

We established that such a course of reaction occurs to an insignificant extent when methyl glucoside is oxidized in cuprammonium solution [19]. The aldehyde and ketone groups formed must oxidize further into carboxyl groups: uronic in the 6-position, nonuronic in the 2- and 3-positions and at the ends of chains in the 1-position.

In the variety of the simultaneously occurring chemical reactions the oxidative breakdown of cellulose under the action of hydrogen peroxide is reminiscent of the breakdown of

medium with hypochlorite, only a negligible amount of nonuronic carboxyls may be formed; none, in fact, can be detected by analysis. In the case of peroxide oxidation in an acid medium, analysis indicates a definite content of nonuronic carboxyls; here, therefore, from the very beginning of the oxidation, we have rupture of the pyran ring, a process which we do not find in the early stages of hypochlorite oxidation.

A second difference lies in the aldehyde content. Oxycelluloses obtained by oxidation with sodium hypochlorite in an acid medium contain a considerable number of aldehyde groups, but in the case of alkaline oxidation the number of aldehyde groups formed is negligible (except when very severe oxidation accompanied by much chain breakdown occurs). No such marked variation in the number of aldehyde groups according to the reaction of the medium is to be observed for hydrogen peroxide oxidation. In order to demonstrate this point, we may compare the ratios of aldehyde to carboxyl groups in the two series of oxycelluloses.

It will be seen from Table 8 that the values of the ratio CHO/COOH for hypochlorite oxidation are widely different for acid and alkaline treatments (the mean values are 1.30 and 0.23 respectively), and that this difference is much less for peroxide oxidation (mean values of 1.06 and 0.73). There is some justification for associating this fact with indications, derived from analyses of the oxycelluloses, of the presence of aldehyde groups formed by the rupture of the 2,3-C-C link.

In this connection, the following peculiarity should be mentioned: if hypochlorite and peroxide oxycellulose preparations having about the same degree of polymerization are compared with one another, it is found that the hypochlorite oxycelluloses contain more oxidized functional groups (the sum of carboxyl and carbonyl groups) (see figure).

From this it may be concluded that the breakdown of the cellulose macromolecule is brought about more readily by the action of peroxide than by the action of hypochlorite. This relation is observed in alkaline, neutral, and acid media. A possible cause of this phenomenon may be the higher temperature employed in the peroxide oxidation (42°, against 20-25° for hypochlorite), leading to a more vigorous attack on the glucoside linkages that have become unstable owing to the proximity of oxidized functional groups. It is more probable, however, that this difference in behavior is caused by this very difference in the content of and character of the aldehyde groups in oxycelluloses produced by the two oxidation processes, and that the temperature factor only intensifies this difference.

It follows, therefore, from a comparison of analytical results that peroxide oxidation of cellulose differs from hypochlorite oxidation with respect to one particular oxidative reaction—the breakdown of a glycol grouping into two aldehyde groupings—which is more in evidence in the first case. This conclusion is based on the greater relative content of aldehyde groups after peroxide oxidation, on the formation of nonuronic carboxyls not only in alkaline, but also in acid media, on the impossibility of finding places for all the nonuronic aldehyde groups at ends of chains, and on the more ready breakdown of oxycelluloses produced by peroxide oxidation. This conclusion is based also on the fact that the splitting of glycols by hydrogen peroxide with formation of two aldehyde groups has been demonstrated for the simplest glycols and follows also from our experiments on the oxidation of methyl glucoside. There are therefore grounds for explaining the facts that we have given from the point of view of this reaction in the case of the oxidation of cellulose with hydrogen peroxide. Nevertheless, such an explanation does not exclude the possibility of the occurrence of other processes leading to similar changes in the oxycelluloses.

In complete absence of catalyst, the oxidation of cellulose by hydrogen peroxide at about 50° proceeds extremely slowly and is qualitatively different from oxidation in presence of Fe^{++} . Very few oxidized groups are formed, and practically all of the carboxyls formed are uronic. Nevertheless, chain-breakdown occurs after a time. Prolonged oxidation with hydrogen peroxide in absence of catalyst leads, therefore, to a fall in viscosity without any appreciable accumulation of functional groups.

SUMMARY

1. A study has been made of the composition of oxycelluloses obtained by oxidation with hydrogen peroxide in acid, neutral, and alkaline media.
2. It has been shown that chemical modification of the cellulose and fall in degree of polymerization occurs at all values of pH, though in varying degree: oxidation proceeds most intensively in strongly alkaline ($\text{pH} > 11$) and in acid ($\text{pH} < 4$) media.

3. In the oxidation of cellulose by hydrogen peroxide the same chemical processes occur as in the oxidation of the simplest sugars, namely: the primary OH groups are oxidized to aldehyde and carboxyl groups; secondary OH groups are oxidized with formation of ketone groups and oxidation of 2,3-glycol groupings with rupture of the ring yielding two aldehyde groups, which may be converted further to carboxyls.

The introduction of a catalyst(Fe^{++}) accelerates the oxidation processes, particularly those leading to rupture of the pyran ring with formation of nonuronic carboxyls.

4. Certain differences are to be observed between the chemical compositions and properties of oxycelluloses obtained by hypochlorite and by peroxide oxidation. The most important cause of these differences appears to be the breakdown of the glycol grouping into two aldehyde groups, a reaction that has not yet been shown to occur in oxidation with hypochlorites.

5. Owing to the occurrence to a marked extent of the latter type of oxidation with rupture of the pyran ring, the variety of new functional groups formed in the cellulose macromolecule during its oxidation by hydrogen peroxide is even greater than in hypochlorite oxidation: under all pH conditions groups will be formed that reduce the stability of the glucoside linkages in acid and alkaline media and so induce chain-breakdown.

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LITERATURE CITED

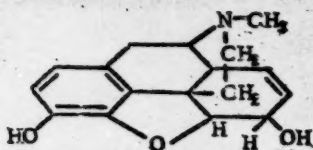
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ALKALOID CHEMISTRY - ITS SIGNIFICANCE, AND ITS IMMEDIATE PROBLEMS*

V. M. Rodionov

The term "alkaloids", proposed in 1818 by Meisner for vegetable bases of complex structure that have powerful physiological effects, quickly received general acknowledgement, for it was in accord with the requirement that new substances should be characterized by their most important attribute. In this case the most important characteristic of the new compounds appeared to be their well marked alkaline properties. Study of the reactions and structures of alkaloids has been of tremendous importance for the development of theoretical and preparative organic chemistry, and it has created several new sections in this subject. The following examples will serve sufficiently well to demonstrate this point.

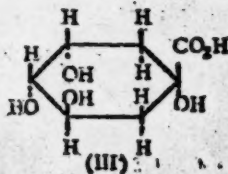
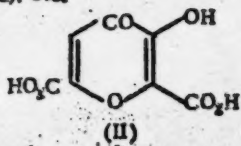
At the very beginning of the nineteenth century, the first alkaloid, morphine (I) was isolated from opium:



Study of the properties of morphine showed that the characteristic pharmacological sedative action of opium is due essentially to the presence therein of morphine. It was by this means that it first became possible to carry out quantitative investigation of the physiological efficiency of this drug. The discovery of such an active compound as morphine was of great significance and gave rise to many investigations of other drugs of vegetable origin and also of the plants themselves.

In 1820 a method was published for the isolation of quinine and cinchonine; the main active principles of another, still more important medicinal preparation—cinchona bark, used in the treatment of malaria. The study of opium and cinchona bark very soon showed that these preparations are complex mixtures of vegetable bases that are fairly similar in structure and that the overall biological and medicinal actions of opium and cinchona bark are in many ways different from those of the individual substances morphine and quinine.

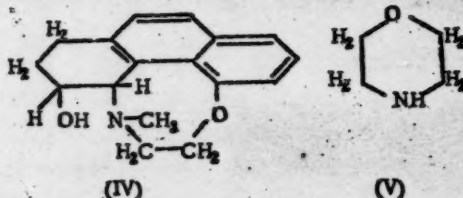
This important observation led to a deeper investigation of the starting materials; methods of isolation and of the further separation of the component parts (the so-called subsidiary alkaloids) were refined, and it was found that each of the complex medicinal preparations, opium and cinchona bark, contain more than 25 different individual substances, sometimes with similar, and sometimes with quite different, physiological properties. The common property of all these compounds was their basic character—the propensity for stable salt formation with both mineral and organic acids. Almost all of the alkaloids that have been isolated from plants are there present as salts, sometimes of very characteristic organic acids: meconic for the opium alkaloids (II), quinic for the cinchona bark bases (III), etc.



* Paper read before a combined session of the Division of Chemical Sciences of the USSR Academy of Sciences and the Uzbek SSR Academy of Sciences on October 25th, 1952 in Tashkent.

The investigation of the chemical composition of opium and cinchona bark led to extensive investigation of plants, particularly poisonous plants, with respect to their content of alkaloids. The number of such compounds began to grow rapidly and has now attained a very large value (more than 1200 individual substances).

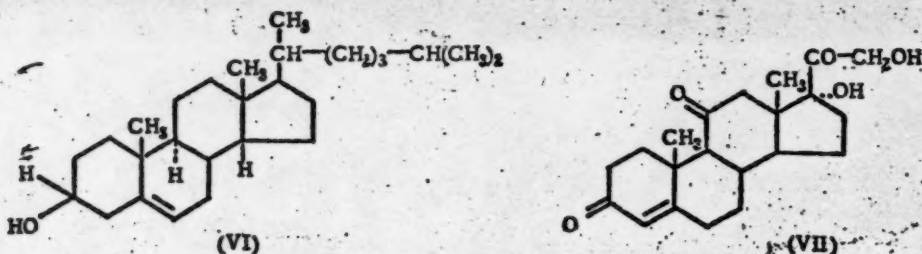
The careful study of the properties and structures of the alkaloids isolated has been found to be particularly valuable and important for the chemistry of heterocyclic compounds. This complicated branch of organic chemistry owes its early successful development largely to results obtained in the investigation of various alkaloids. A very large number of important syntheses were the results of early attempts to make an approach to the syntheses of morphine and quinine. The preparation, for example, of such an interesting heterocyclic compound as morpholine (V) was prompted by the desire to confirm one of the early incorrect formulas proposed for morphine (IV):



(Knorr, 1903).

Morpholine was later found to be a very valuable starting material for the preparation of pharmacological preparations, and also for the synthesis of some basic dyes (Rosol Red and Scarlet).

The establishing of the phenanthrene ring system as the basis of the morphine molecule resulted in an exhaustive study of the properties of phenanthrene itself and of its derivatives, several general syntheses of these substances being developed at the same time. This made it possible later to determine the structures of the biologically important sterols, which include compounds such as cholesterol (VI), coprosterol, phytosterol, ergosterol, vitamins of the D group, bile acids, sex hormones, hormones of the adrenal cortex, digitalis glucosides, and many others. Investigations in this field led to the synthesis of many valuable preparations of the sex hormone type and also, quite recently, to the elucidation of the structure and to the synthesis of such an important medicinal preparation as cortisone (VII)*.



Already immediately after the discovery of the vegetable bases, systematic work began on the preparation of active substances that could replace morphium and other alkaloids. Such attempts were completely successful in many cases, and some of the preparations synthesized (for example, demerol and its analogs, also compounds of the 4-piperidinol type, particularly Soviet promedol**) are considerably more active as sedatives than morphine, and may displace morphine and pantopon, for preliminary investigations indicate that they are not habit-forming. In this respect, caution is necessary, for over-enthusiasm for certain new drugs has frequently reacted unfavorably on treatment. It will be sufficient to refer to the many unpleasant consequences of the incorrect use, at one time, of the drug sulfidine and, possibly of sulfamide drugs in general; they are frequently taken without suitable medical advice.

* Cortisone is able to relieve suffering due to rheumatic arthritis, rheumatic fever, and such severe infections as pneumonia, it is, at the present time, one of the most extensively studied drugs.

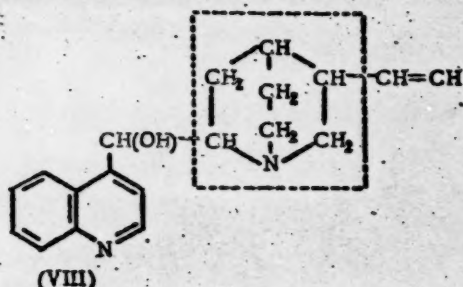
** Synthesized by I. N. Nazarov (Institute of Organic Chemistry of the USSR Academy of Sciences).

Feverishly hasty application of new discoveries is very characteristic of our times, a statement that is true, of course, not only of drugs. The typical attitude to new things in the last century was quite different. For the purpose of comparison we will take two examples. In 1784 the first patent for puddling was taken out, and in 1818 the technical difficulties of the process were overcome by the invention of a suitable hearth, and more vigorous propaganda for the desirability for puddling was begun, but only in 1849, i.e. 65 years after the discovery of the method, did the process come into regular use.

A similar example may be cited from the manufacture of pharmaceuticals. In 1860 a method for the preparation of salicylic acid was discovered, and in 1873 all the technical difficulties had been overcome and the synthesis of this important medicinal and technically necessary product was introduced into industry. Nevertheless, toward the end of the nineties of the last century it was still possible to find statements in pharmaceutical literature to the effect that certain derivatives of synthetic salicylic acid are inferior with respect to quality and physiological action to the natural compounds. This cautious attitude has now completely changed: quite frequently in foreign countries, a newly discovered article will be sold before it has been carefully tested and shown to be sound, and a new drug is sometimes put into use without even a preliminary clinical test.

The study of the subsidiary opium alkaloids contributed a great deal to the development of isoquinoline chemistry, and syntheses were worked out for many natural alkaloids: papaverine, narcotine, narceine, and others. The difficulty encountered in the elucidation of the structural formula of morphine itself is particularly worthy of note. Almost 130 years were required for the precise determination of the structure of the complex and labile molecule of this important alkaloid, and only quite recently has the total synthesis of this compound, which confirmed the structural formula proposed for it in 1935, been effected.

Of no less significance for the development of the chemistry of heterocyclic compounds and of medicinal products was the study of the structure of quinine (VIII) and subsidiary alkaloids derived from cinchona bark.



(R = H in cinchonine and OCH_3 in quinine. The quinuclidine ring system is indicated by the broken line.)

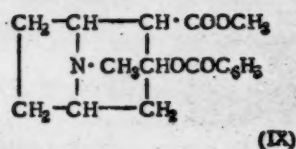
The chemistry of two very important heterocyclic systems, quinoline and quinuclidine, was brought into being. These two compounds form the basis of many medicinal preparations. Among the derivatives of quinoline it is sufficient to mention plasmocide, plasmochin, and atophan. Valuable drugs are obtained also from quinuclidine. The preparation of this last compound is of interest, for it made possible one of the most brilliant syntheses of recent times: the synthesis of optically active quinine, in no way different from the natural product.

It may be appropriate here to pass an opinion on the practical value of such brilliant syntheses as those of quinine and morphine. While we have readily accessible natural sources for these compounds—for example, opium and cinchona bark, containing up to 10% or more of these alkaloids, which are readily isolated—the question of the practical expediency of the synthetic preparation of quinine and morphine is scarcely worth thinking about. In this case nature works more cheaply, and it is senseless to compete with it. The question of the improvement of natural preparations by synthesis must, however, be regarded quite differently. Great efforts have been made by many workers to eliminate the bitter taste of quinine, while preserving its antimalarial properties. This was achieved completely by the preparation of euquinine and aristoquine. Interesting work has been done also on the synthesis of ethers of morphine and cupreine, resulting in such important products as codeine, diionine, optichine, etc. It is worthy of mention that the

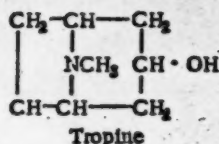
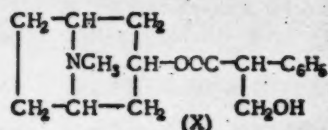
preparation of codeine from morphine has been known for a considerable time, but only in the twenties, in our own country, was the best synthesis for this alkaloid found.

Early attempts to synthesize quinine, the structure of which had not been established, gave industry synthetic dyes, and an attempt to prepare this substance by another method resulted in methods for the preparation of pyrazolone derivatives, which have attained considerable importance for pharmacological chemistry (antipyrine, pyrazolone, analgine, etc.) and also for the preparation of fast yellow and red dyes.

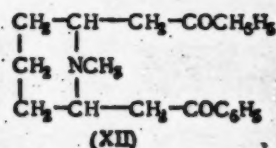
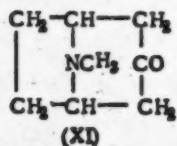
The examples cited are sufficient to show what influence the study of these two very important alkaloids has had on the development of preparative organic chemistry, particularly that associated with the synthesis of medicinal substances, but it will be of value to consider yet another alkali namely cocaine (IX):



The investigation of the structure and properties of this preparation, which was so highly valued by the Peruvian Indians, has formed the basis for the syntheses of anesthetic substances that can replace cocaine; these possess its high qualities, but not its harmful effect on the nervous system. It was found that for a compound to have a local anesthetic action both a substituted amino group and an acylated (generally benzoylated) hydroxy group must be simultaneously present in the molecule. The numerous important preparations of this type include anesthine, alipine, stovaine, dolantin, and naphthocaine. At the same time the peculiarities of molecules having mydriatic and antispasmodic action were established [atropine (X), homatropine, eumydrin, etc.]. Homatropine is the mandelic ester of tropine, and eumydrin is the quaternary methonitrate of atropine:



Questions concerning the nature of the alkaloids and their functional significance in the life of plants have given rich material both for chemical investigations and for investigations of a botanical and physiological nature. Investigations into phytochemical synthesis are particularly interesting: they show that many complex heterocyclic systems can be synthesized under conditions approximating to those found in nature—at ordinary temperature and pressure, making use only of changes in the pH of the medium. Many very important compounds have been prepared by this method: it will be sufficient to mention such interesting and important substances as tropinone (XI), the starting substance for the synthesis of tropinone derivatives, and lobelanine (XII) (stimulatory substance):



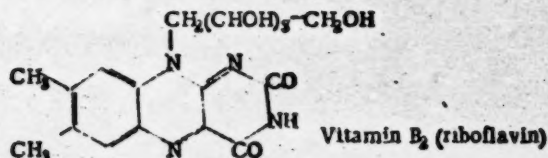
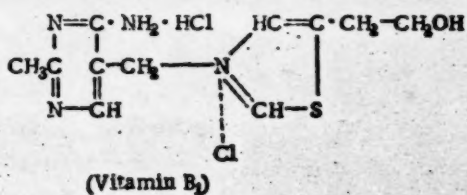
From what we have said, a clear picture will be formed of the influence that study of alkaloid chemistry has had on the development of organic chemistry—an influence that has not lost its significance even now: in

fact, in many countries at the present time intensified study of new alkaloïd-containing plants is proceeding with the object of separating their biologically active principles. It should be mentioned here that our own country is taking a very active part in this work: the work of our investigators has made a considerable contribution to this branch of organic chemistry, and the richness of our flora gives promise of many further successes.*

It will be seen from this short sketch that, as a result of investigations into alkaloïd chemistry, a large amount of material has been obtained which has contributed much that is necessary and useful for the development of theoretical organic chemistry and for the development of new pharmaceutical substances. However, many important questions still remain unsolved. There is still no generally held opinion concerning the functional significance of alkaloïds for the plant. The elucidation of this important matter demands much coordinated work of a profound nature by chemists and physiological botanists. The attempts, as yet very modest, to study the presence of alkaloïds during various growing periods of the life of the plant must be continued.

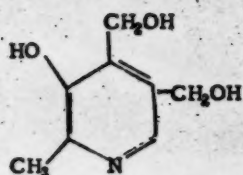
Apart from theoretical importance, these investigations may also have a practical result: they will establish the time at which an important alkaloïd may be isolated in the greatest possible yield, and the part of the plant from which it should be obtained. The work on the phytochemical synthesis of alkaloïds or heterocyclic systems in general is very important, for it may supply the key to the understanding of the way in which these complex substances are synthesized in the living organism.

An enormous number of isolated alkaloïds have still not been sufficiently investigated from the chemical and biological points of view. The structures of many preparations that have long been in use in medicine have not been completely elucidated. Many of these substances have not been studied thoroughly from the pharmacological side. A medicinal preparation that is very valuable for the treatment of one pathological condition may be harmful in another respect. Precipitant application of new drugs is not a rare occurrence. Often, the study of the biological action of the complex of active principles in a plant is inadequate. Whereas at the end of the Eighteenth Century the presence of vegetable acids was regarded as characteristic for a plant, since the beginning of the Nineteenth Century considerably less attention has been devoted to the acid composition of alkaloïd-bearing plants, and, at the best, in studies of the compositions of these plants, the vegetable acids have been isolated; their elementary analysis has been made, in some cases they have been synthesized, and nothing further has been done. It is necessary to study the acid composition also from the biological point of view. It is difficult to believe that these substances are indifferent for the life of the plant and for the living organism. It is quite possible that they will be found to be important both from the biological and from the pharmacological point of view. It should be remembered that such acids as nicotinic, pantothenic, p-aminobenzoic, ascorbic, and even some acids of the aliphatic series, have been found to possess vitamin character. It must not be forgotten that many branches of chemistry are closely interwoven, and if new terms, such as vitamin and antibiotic, had not been introduced into chemistry, then compounds such as vitamins of the B, B₁, B₂, and B₆ groups, and antibiotics such as penicillin, streptomycin, and even chloromycetin, would have been included in the alkaloïd groups.

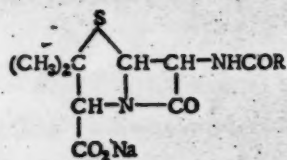


* The investigations of our workers into the chemistry of alkaloïds are very extensive and varied; they should be considered in a special article.

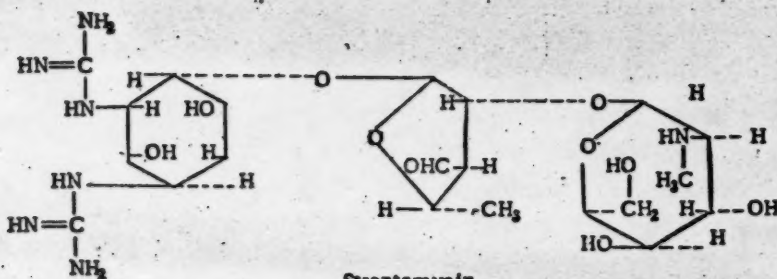
Antibiotics



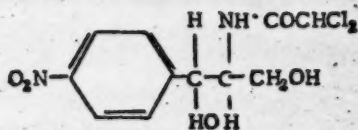
Vitamin B (pyridoxine, adermin)



Penicillin



Streptomycin



Chloromycetin (chloramphenicol)

For the investigators of our country who are working on questions in alkaloid chemistry there is a very large number of problems that remain unfinished, or have not yet been tackled. Also, the investigation of the alkaloid-bearing plants of our Central Asian republics is not completed. The same may be said concerning our central regions: by way of example it may be pointed out that up to now inadequate investigation has been given to plants of the greater celandine type, to hellebores, and to many others that are characteristic of the central belt of European Russia. There is also an enormous wealth of plants in the Far East and the Ussury province which await their turn and have as yet received practically no attention.

The possibility of propounding and solving such difficult problems is becoming ever greater, for with every year the more remote regions of our fatherland become more and more enriched in universities and research institutes.

BRIEF COMMUNICATIONS

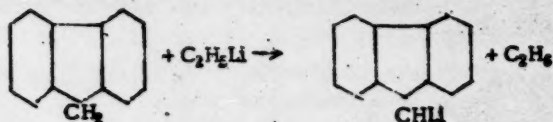
CRYSTALLINE ORGANOLITHIUM COMPOUNDS.

9-FLUORENYLLITHIUM, PHENYLETHYNYLLITHIUM.

T. V. Talalaeva and K. A. Kocheshkov

The method we have developed [1], for the preparation of crystalline ethyllithium and, therefore, of pure solutions of this substance, free from extraneous matter, has found wide application for the preparation of crystalline aromatic organolithium compounds [2], and aralkyl compounds [3], by metal-metal, or metal-halogen replacement with organoantimony, organobismuth, and halogen-substituted compounds.

In the present investigation on the preparation of crystalline fluorenyllithium and phenylethynyllithium, the reaction of hydrogen-metal exchange (the Shorygin reaction) was used [7]:



The metalation of fluorene by ethyllithium (in benzene and ligroin) has been described previously and did not lead to the isolation of individual fluorenyllithium; the authors [4] gave neither the yield nor the analysis of the substance. The reaction of ethyllithium in ether solution (in which it is rapid) [5] and in xylene [6] (18 hours, 80% yield) has been described; again no crystalline substance was isolated. Hence, as we were carrying out a systematic study of crystalline organolithium compounds, we considered it necessary to obtain an individual preparation of fluorenyllithium (a representative of the cyclopentadiene-fluorene group of compounds [7]). Still less is known of isolated representatives of the acetylene series. The formation of phenylethynyllithium in ether solution from phenylacetylene and butyllithium (or phenyllithium) has been demonstrated indirectly by the formation of phenylpropionic acid. In the present investigation we have prepared crystalline phenylethynyllithium and described its properties:



All operations in the preparation of crystalline fluorenyllithium and phenylethynyllithium were carried out under the conditions and in the apparatus that have been described previously [1, 2, 3].

EXPERIMENTAL

9-Fluorenyllithium

Ethyllithium (1.15 g; 1 mol.) in benzene (30 ml) was introduced into the apparatus previously described [2], and a solution of fluorene (5.5 g; 1 mol. + 0.2 g excess) in hot benzene (15 ml) was added. Immediately on mixing the solutions, there was an orange coloration and evolution of ethane. The reaction proceeded on its own at room temperature (23-24°) for seven hours (steady evolution of gas). Orange crystals of fluorenyllithium separated. In order to complete the reaction the mixture was heated at 75-78° for 3 hours 30 minutes, until ethane ceased to be evolved. The warm solution was filtered under nitrogen. The residue was washed on the filter, once with benzene and three times with dry pentane, was dried in a stream of nitrogen (in the apparatus already described [2]), and was sealed in tubes. The yield was quantitative.

Found %: Li 3.88; 3.82
C₁₉H₉Li. Calculated %: Li 4.03

Crystalline fluorenyllithium is a yellow substance having a slight orange tinge; it is soluble in ether and difficultly soluble in benzene and hexane. It is infusible, does not inflame in air, but is readily decomposed with decolorization. It may be preserved unchanged for at least a year when sealed in tubes under pure dry nitrogen.

It gives a strong test with Michler's ketone (it is most convenient to take ether solutions of fluorenyllithium).

Phenylethynyllithium

Ethyllithium (0.49 g; 1 mol.) in benzene (13 ml) was placed in the apparatus (described previously [2]). A dropping funnel was attached to the apparatus, and from this, with shaking, phenylacetylene (1.5 g, 1 mol.) was added gradually. A vigorous reaction ensued, with rise in temperature, evolution of ethane, and formation of a white precipitate of phenylethynyllithium. The reaction rapidly came to an end. The apparatus was left until next day, when the precipitate was filtered off under a pressure of nitrogen (this filtration must be carried out on a wide porous-glass filter, as it is otherwise very slow). The precipitate was washed three times with pentane, dried at 35-45° for one hour in a stream of nitrogen, sealed in tubes, and analyzed. The yield was quantitative.

Found %: Li 6.40; 6.41

C_8H_5Li . Calculated %: Li 6.43

Crystalline phenylethynyllithium is a white infusible substance. In air it does not inflame, but it rapidly decomposes. It is soluble in ether, difficultly soluble in benzene or hexane. It reacts vigorously with water and with alcohol. It gives a color reaction with Michler's ketone.

SUMMARY

1. The hydrogen-metal exchange reaction (Shorygin's reaction) has been employed for the synthesis of crystalline fluorenyllithium from fluorene and ethyllithium.
2. The same reaction has been used for the synthesis of crystalline phenylethynyllithium from phenylacetylene and ethyllithium.

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* See Consultants Bureau English translation, page 113.
** See Consultants Bureau English translation, page 293.

OBITUARY

ACADEMICIAN VLADIMIR ALEKSANDROVICH KISTYAKOVSKY

On October 19th, 1952, the death occurred, after a severe illness, of Academician Vladimir Aleksandrovich Kistyakovsky, one of the founders of modern physical chemistry and a distinguished scientist who has enriched chemical science by many original and profound investigations and who has trained several generations of workers in science and technology. He was in his eighty-eighth year.

The beginning of V.A. Kistyakovsky's scientific activities practically coincided with the birth of the theory of electrolytic dissociation, and his further work contributed in an exceptional degree to the development of several very important fields of physical chemistry, particularly electrochemistry.

V.A. Kistyakovsky gave an original theoretical treatment of chemical reactions in solution and established laws relating to the capillary rise of liquids at their boiling points. The investigations of Vladimir Aleksandrovich on complex cations, on methods of determining electrode potentials, on the passivity and corrosion of metals, and in colloid chemistry, photochemistry, and stoichiometry; his formulas for latent heats of vaporization and for the dependence of vapor pressure on pressure at near the boiling point; and his various other works—all these will remain for ever in the treasure house of science.

The development of the film theory of the passivity of metals, which was originated by V.A. Kistyakovsky in 1909, led him to the formulation in 1925, of an original film theory of metal corrosion, which has shown itself to be a reliable means of ascertaining the essential features of the complex phenomena of metal corrosion and has given clear indications of the directions to be taken by future investigations in this field.

At the basis of V.A. Kistyakovsky's film theory lies the hypothesis that a metal surface in moist air is covered by a film. The structure of this film is different for different metals: it varies from a molecularly adsorbed layer to a layer of oxides, in the case of readily oxidizable metals. The transition of a metal from the passive condition (in which it has a continuous surface film of oxides) to the active state is associated with the appearance of pores in the film and is not conditioned necessarily by the complete removal of the oxide film from the surface.

The corrosion of metals in moist air and in solutions of electrolytes (if oxides can exist under the conditions under which the process is carried out) proceeds mainly on account of local currents flowing between parts of the oxide film, occlusions in the surface of the metal, and the metal itself. Oxygen and carbon dioxide serve as depolarizers for the local currents.

V. A. Kistyakovsky regarded the rusting of iron in a profoundly dialectical fashion, treating it as a complex process in the course of which the local currents break up the film, forming pores. Molecular forces also free the metal surface from the film, causing the film to come away by bringing about its crystallization. On the other hand, electrical forces re-create the film in the bared places (by means of the process $n\text{Fe} + m\text{OH}^- \rightarrow \text{Fe}_n(\text{OH})_m + m\text{e}$). The process proceeds continuously: in effect we have disruption of the film, its crystallization, and erosion of the iron at the anodes of the local currents; and rust therefore accumulates.

The further advance of science, armed with new and ever more perfect methods of investigation, does not lead to the rejection of V.A. Kistyakovsky's film theory of metal corrosion, but, on the contrary, leads to its consolidation and to a call for its further development.

V.A. Kistyakovsky's investigations have always been devoted to the theoretical and experimental study of questions having great significance for the national economy of the U.S.S.R. He published more than 120 papers of the highest scientific importance during more than sixty years of scientific activity.

In 1916 V.A. Kistyakovsky published the first Russian textbook on electrochemistry; it was packed with new ideas and original methods. In 1926, V.A. Kistyakovsky's textbook, "Applied Physical Chemistry" was published.

The scientific services of V.A. Kistyakovsky were marked by his election in 1925 as Corresponding Member and in 1929 as Active Member of the U.S.S.R. Academy of Sciences.

In the Laboratory for Colloids and Electrochemistry and the Institute for Colloids and Electrochemistry of the U.S.S.R. Academy of Sciences (founded by V.A. Kistyakovsky and directed by him until 1939), Vladimir Aleksandrovich with his students and collaborators, carried out extensive investigations on metal corrosion and electrocrystallization. After the conversion of the Institute for Colloids and Electrochemistry into the Institute of Physical Chemistry of the U.S.S.R., Vladimir Aleksandrovich directed the Laboratory for Colloids and Electrochemistry in this Institute until his death, so acting as leader of scientific work on passivating films on metals and on the motoelectric phenomena of potential changes at electrodes resulting from their movement in electrolyte solutions.

Vladimir Aleksandrovich Kistyakovich began his activity as a teacher in 1897, at St. Petersburg University, where, for the first time in Russia, he gave lecture courses in electrochemistry and photochemistry. During his period at the St. Petersburg Polytechnical Institute, he instituted the first big laboratory in Russia devoted to work on physical chemistry and electrochemistry.

During his teaching career (1897-1934), Vladimir Aleksandrovich trained many hundreds of metallurgists and chemists, to whom he lectured on physical chemistry, electrochemistry, thermodynamics, and inorganic chemistry.

From 1934 to 1939, V.A. Kistyakovsky was a member of the Moscow Soviet of Worker-Peasant and Red-Army Deputies.

The government of the U.S.S.R. set a high value on V.A. Kistyakovsky's services to science and rewarded him on two occasions with the Order of Lenin.

Vladimir Aleksandrovich Kistyakovsky, scientist patriot, devoted son of the Fatherland, has, by his sixty years of scientific activity, and his forty years of fruitful work, devoted to the preparation of cadres of scientific and technical workers, shown an example of self-effacing and fruitful service to science and to the Fatherland.

The bright image of V.A. Kistyakovsky will live on in the hearts of all who knew him to the ends of their days. Vladimir Aleksandrovich Kistyakovsky's scientific ideas will, for a long time yet, continue to encourage the further development of physical chemistry, and his name will be preserved forever in the history of Soviet chemistry.

CURRENT EVENTS

AWARD OF D. E. MENDELEEV PRIZES FOR 1952

The Presidium of the U.S.S.R. Academy of Sciences has awarded D.E. Mendeleev prizes for the 1952 contest as follows.

A prize of 20,000 roubles to G.V. Akimov, Corresponding Member of the U.S.S.R. Academy of Sciences, E.N. Paleolog, Candidate of Chemical Sciences, and G.B. Klark, Candidate of Technical Sciences, for a series of investigations on the electrochemistry of protective films on metals.

A prize of 10,000 roubles to G.S. Zhdanov, Doctor of Physicomathematical Sciences, and Z.V. Zvonkova, Candidate of Chemical Sciences, for the work, "The Crystal Chemistry of Metal Thiocyanates".

A prize of 10,000 roubles to A.B. Nalbandyan, Doctor of Physicomathematical Sciences, and V.V. Voevodsky, Candidate of Physicomathematical Sciences, for the work, "The Mechanism of the Oxidation and Combustion of Hydrogen."

A prize of 10,000 roubles to A.M. Rubinshtein, Doctor of Chemical Sciences, for the work, "The Physical Structure and Properties of Catalysts for Organic Reactions".

The investigations of G.V. Akimov, Corresponding Member of the U.S.S.R. Academy of Sciences, and his co-workers on the electrochemistry of protective films on metals are of great scientific and practical importance. The question of the nature of oxide films, which is extremely important for the theory of metal corrosion, has been approached from entirely new angles in G.V. Akimov's investigations. The great effect of surface oxide films on the rate of metal corrosion has been known for a long time. This phenomenon was first investigated and described by M.V. Lomonosov in his work on the action of nitric acid on iron. The fruitful work of the late Academician Kistyakovskiy and of the late Professor P.D. Dankov, on protective films leading to the creation of the film theory of corrosion, comprises an important stage in the study and estimation of the significance of oxide films on the corrosion behavior of metals.

In the investigations entered for the contest, which were carried out in conjunction with G.V. Klark and E.N. Paleolog, G.V. Akimov developed the idea of the electrochemical heterogeneity of protective films, proved this hypothesis experimentally, and presented many important facts of scientific and practical value.

The investigations were carried out by elegant electrochemical methods: in many cases novel apparatus, constructed by G.V. Akimov and his co-workers, was used.

In the paper, "Introduction to the Electrochemistry of Protective Films", which was published in "Progress of Chemistry", Vol. 15, No. 3, p. 353 (1947), G.V. Akimov rejected W. Müller's concept of the oxide film on a metal as a normal microgalvanic system. He exposed the fundamental error made by Müller, namely the consideration of only the ohmic resistance of the system and complete neglect of polarization.

On the basis of the results of experimental investigations carried out in conjunction with E.N. Paleolog, G.V. Akimov developed the concept of the electrochemical structure of protective films and of the presence on them of regions of three sorts: cathodic, anodic, and electrochemically neutral. By means of these investigations a new branch of corrosion science was discovered: the electrochemistry of protective films.

Among the succeeding investigations of G.V. Akimov and co-workers, that carried out, in conjunction with E.N. Paleolog on the electrochemical structure of protective films on metals (State Defense Press, 1950), presents great scientific interest. In the course of this work the authors developed a simple method for detecting the electrochemically active regions of the protective film. They made use of the principle of cathodic polarization of the samples in a solution containing a special indicator, which revealed quite clearly that a phosphate film on iron may be divided into cathodic, anodic, and inert regions. This work is not only of scientific interest, but also of great practical interest.

Further investigations of G.V. Akimov and E.N. Paleolog (Transactions of the Institute of Physical Chemistry of the U.S.S.R. Academy of Sciences, 1951, Collected Volume No. 1), were devoted to a study of oxide films on aluminum (the electrochemical behavior of aluminum in presence of various anions, and the investigation of its electrode potentials), and they discovered a number of laws applicable to this system.

The authors made wide use of the polarization diagram method, which enabled them to discover a number of interesting phenomena. They found that aluminum having an oxide film of low conductivity and immersed in a solution constitutes a microgalvanic system and that the nature of the anions present in the solution may have an important effect only on the anode process. It was shown that aluminum, in presence of SO_4^{2-} and NO_3^- ions is very strongly polarized anodically, whereas in presence of halide ions the polarization of aluminum is very slight.

When we consider the contemporary importance of aluminum in aviation and the consequent exceptional importance of studies of the causes of corrosion damage to aluminum and the mechanism of its development, the great practical value of these investigations becomes clear.

The thorough investigations of G.V. Klark and G.V. Akimova described in their "Investigations of Protective Films on Metals by the Conductivity Method" (U.S.S.R. Academy of Sciences Press, 1952), are also of great practical importance. The significance of the extensive experimental material obtained by the aid of the apparatus developed by these authors for the measurement of the resistance of surface films on metals extends far beyond the question of checking the applicability of this apparatus. It presents interest on its own account in relation to the determination of the electrical properties of various films on various metals. For the first time a wide characterization of the physicochemical properties of various films on almost all metals (except the alkali metals) is presented.

It should be noted that among a number of laws discovered by G.V. Akimov and his co-workers, and experimentally confirmed by them, there is the relation observed between the position of the metal in D.I. Mendeleev's periodic system of the elements and the electric properties of the films — in particular, the effect of the film on the electrode potential of the metal.

In "The Crystal Chemistry of Metal Thiocyanates" G. S. Zhdanov and Z. V. Zvonkova have generalized a large volume of experimental material obtained as a result of X-ray investigations of the structures of simple and complex metal thiocyanates and have systematized data on their chemical structures on the basis of chemical bond types.

A number of new facts are given regarding the chemical structures of 1) the thiocyanato group; 2) ionic crystals of metal thiocyanates; 3) molecular thiocyanato compounds; 4) thiocyanato compounds having hydrogen bonds; 5) complex thiocyanates of transitional metals, and also of metals of the second group of the periodic system that are most prone to four-fold and six-fold coordination round the complex forming metal.

On the basis of analysis and comparison of the crystal structure of various metal thiocyanates, and also of cyanides and halides, the authors have established a number of crystallochemical relations that are of great importance for the crystal chemistry of simple and complex inorganic compounds.

The purposeful work carried out by the authors over many years forms an important contribution not only to crystal chemistry, but also to the chemistry of complex compounds.

The monograph of A.B. Nalbandyan and V.V. Voevodsky, "The Mechanism of the Oxidation and Combustion of Hydrogen" gives an exposition of the fundamental concepts of the modern theory of branched chain reactions and also of the method of application of this theory to concrete problems, the oxidation of hydrogen being taken as example. The theory is applied to the setting up and substantiation of the reaction mechanism, the determination of the limits of ignition, analysis of the question of heterogeneous chain rupture, and so on, and the whole of the factual material is analyzed on the basis of these theoretical concepts. Formulas are derived for the dependence of the position of the ignition limits on the treatment given to the walls of the vessel, the composition of the mixture, inert and chemically active additives, the action of light, and additions of free atoms.

The phenomena occurring when a mixture burns within the "peninsular" of ignition (kinetics of the nonstationary process, the period of induction, the sharp rise in the concentration of active particles in the reaction zone), are analyzed. The question of the slow oxidation of hydrogen and its transition into an explosion at pressures near to that of the atmosphere is examined. The dependence of the character of the reaction and of the ignition on the treatment given to the vessel walls is demonstrated and explained, and in particular it is shown that when the explosion is of a thermal nature in clean vessels, in which the rate is very high, then in vessels that have been treated with salts, in which the rate is 100-1000 times lower, the explosion proceeds by chain mechanism. All the experimental data examined in the book are in quantitative agreement with theoretical calculations, and it has been possible to determine with high accuracy the rate constants of all the elementary processes entering into the mechanism of the oxidation of hydrogen. By the use of these values it is possible to calculate beforehand the kinetics of the hydrogen oxidation process in vessels of various form and dimensions (and made of various materials) over a very wide range of pressure and temperature, i.e., to control the oxidation process.

The monograph contains a large amount of experimental material obtained by the authors and it presents a detailed examination and analysis of the whole complex of complicated factors that are characteristic for branched chain reactions. The work is a major contribution to the study of the kinetics and mechanism of chemical reactions.

In A.M. Rubinshtein's "The Physical Structure and Properties of Catalysts for Organic Reactions", an extensive field is covered. The author has studied the relation between the structure of catalysts as revealed by X-rays and their catalytic activity, the dispersity of the sample or the parameters of its crystal lattice (rarely both of these characteristics simultaneously) being determined by X-ray analysis. In individual cases the phase composition was studied also. The greater part of the data refer to the dehydrogenation and hydrogenation of organic compounds on metals (nickel, cobalt, platinum, and palladium).

A number of investigations are devoted to the dehydration and dehydrogenation of alcohols on magnesium oxide, titanium dioxide, and aluminum oxide. A somewhat isolated position is occupied by data on the ketonization of acids on calcium and barium carbonates.

The author has been carrying out these investigations for more than fifteen years. The most systematic study has been devoted to the relation between X-ray dispersity and catalytic activity, and in a number of cases optima have been observed in the microcrystal dimensions and the effect of interatomic distances in the catalysts on their activity and selectivity in organic reactions has been noted.

The investigations are devoted to a problem of present-day importance and fall in with the line of work of the leading school of Soviet organic catalysis headed by Academician N.D. Zelinsky. A.M. Rubinshtein and his co-workers have been responsible for a considerable proportion of the work carried out in the Soviet Union on the X-ray-structure analysis of catalysts.

FROM THE COMMITTEE ON THE DEVELOPMENT OF THE SCIENTIFIC HERITAGE OF A. M. BUTLEROV AND THE PUBLISHING OF HIS WORKS

The committee of the Division of Chemical Sciences of the U.S.S.R. Academy of Sciences on the development of the scientific heritage of A.M. Butlerov and the publishing of his works appeals to all organizations and individuals to inform the Committee of any material in their hands relating to the life and activities of Academician A.M. Butlerov and also to his letters to S.T. Akhakov, P.P. Alekseev, A.I. Pazarov, F.F. Beilstein, N.N. Beketov, P.D. Boborykin, I.A. Polzani, A. Crum-Brown, F. Vroblevsky, A. Burtz, N.A. Golovkinsky, G.G. Gustavson, A. Ya. Danilevsky, A.M. and K.M. Zaitsev, N.N. Zinin, I.A. Kablukov, M. Ya. Kittary, K.K. Klaus, M.A. Kovalevsky, D.P. Konovalov, N.I. Lavrov, Yu. V. Lermontova, M.D. Lvov, V.V. Markovnikov, D.I. Mendeleev, N.V. Nasonov, F.V. Ovsyannikov, A.N. Popov, I.M. Sechenov, A.V. Sovetov, A.S. Famintsyn, F.M. Flavitsky, A.I. Khodnev, L.N. Shishkov, C. Schorlemmer, A.P. Eitekov, E. Erlenmeyer, A.I. Jacobi and others.

All communications should be sent to the Committee's address (Moscow, B. Yaluzhskaya, 31. The Division of Chemical Sciences of the U.S.S.R. Academy of Sciences).

